

Rotational excitation of OH in collisions with CO, N₂, and CO₂

Citation for published version (APA):

Beek, van, M. C., Schreel, K. R. A. M., & Meulen, ter, J. J. (1998). Rotational excitation of OH in collisions with CO, N₂, and CO₂. *Journal of Chemical Physics*, 109(4), 1302-1309. <https://doi.org/10.1063/1.476680>

DOI:

[10.1063/1.476680](https://doi.org/10.1063/1.476680)

Document status and date:

Published: 01/01/1998

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Rotational excitation of OH in collisions with CO, N₂, and CO₂

M. C. van Beek, K. Schreel, and J. J. ter Meulen

Molecular and Laser Physics, University of Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands

(Received 24 December 1997; accepted 14 April 1998)

Relative state-to-state cross sections are obtained for OH colliding with CO, N₂, and CO₂. Hexapole state selection is used to prepare a beam of OH molecules in the upper Λ -doublet component of the lowest rotational state. The collision induced rotational energy transfer is monitored state selectively by means of LIF (laser induced fluorescence) spectroscopy. A study is made of the symmetry effects in the obtained cross sections. The results are compared with previously reported cross sections for Ar, He, and H₂. A general propensity is found for parity conserving transitions to the $\Pi_{3/2}$, $J = \frac{5}{2}$ and $\Pi_{1/2}$, $J = \frac{1}{2}$ states. © 1998 American Institute of Physics. [S0021-9606(98)00828-9]

I. INTRODUCTION

In the last decade a number of state-to-state scattering experiments has been reported on rotational excitation of diatomic molecules. Because the initial state of the molecules studied is well defined and the outcome of the collision is monitored state selectively, these measurements allow for a detailed comparison with theory. The first experiments on rotational excitation, mainly on collisions of closed shell diatomic molecules with rare gas atoms, are described by Levine and Bernstein.¹ In recent years rotational excitation of open shell diatomic molecules in collisions with rare gas atoms have been well studied,²⁻⁶ and also a number of experiments on free radicals colliding with H₂ has been performed.⁷⁻⁹ Recent reviews of this field can be found in Refs. 10 and 11. Recently we reported measurements on the state-to-state scattering of OH ($X^2\Pi$) by He, Ar, and H₂.^{2,7} The obtained symmetry resolved cross sections are in very good agreement with quantum-mechanical calculations based on *ab initio* potentials.^{12,13} The goal of the present experiment is to get insight in the mechanisms governing the more complex scattering of OH by CO, N₂, and CO₂. We have chosen these collision partners because of their relevance in combustion^{14,15} and atmospheric processes.¹⁶ Another reason to choose these molecules is the question whether the substantial differences in the potential-energy surfaces (PES) describing the collisions with these molecules are manifested in the rotational and symmetry dependence of the state-to-state cross sections.

One experiment on rotational excitation of OH ($X^2\Pi$) colliding with N₂ and CO has been reported so far by Sonnenfroh *et al.*¹⁷ They measured the energy dependence of the cross sections, but were unable to prepare the OH molecules in a single Λ -doublet state. As a consequence, their results are symmetry averaged with regard to the initial state. Nevertheless, Sonnenfroh *et al.* observed a preference for excitation to high rotational $\Pi_{3/2}$ states of *e* symmetry in collisions with N₂, while no preference was found in collisions with CO. Moreover, it was found that the cross sections for rotational excitation in collisions with N₂ and CO show only minor differences despite the strong differences in PES's. The OH-CO PES has two van der Waals wells¹⁸ and in

addition a chemically bonded well¹⁹ which describes HOCO complex formation, while the OH-N₂ PES is mainly repulsive. Furthermore the long-range part of the potential of OH-CO is dominated by the dipole-dipole interaction, while the OH-N₂ system is governed by the dipole-quadrupole interaction at long distances. Quasi classical *ab initio* calculations on state-to-state scattering of OH by CO have been performed by Kudla *et al.*¹⁸ No experimental or theoretical studies have been reported thus far on state-to-state scattering of OH ($X^2\Pi$) by CO₂. State-to-state collisions of vibrationally excited OH with N₂ have recently been studied by Crosley.²⁰ He measured collision rates of OH ($X^2\Pi$, $v=1$) scattered by N₂ in a pump-probe experiment.

The scattering of an open shell diatomic molecule like OH by a structureless particle is usually described by considering the symmetry of the electronic wave function. Because all three atoms lay in one plane, the total wave function can be either symmetric (A') or antisymmetric (A'') with respect to reflection in this plane. In the symmetric case the open electronic orbital of OH is oriented in the atomic plane, and in the antisymmetric case perpendicular to this plane. One can construct a separate potential-energy surface (PES) for both symmetries, $V_{A'}$ for the symmetric case and $V_{A''}$ for the anti-symmetric case. Alexander²¹ has shown that for pure Hund's case (a) diatomics, the sum of these potentials $V^+ = \frac{1}{2}(V_{A'} + V_{A''})$ describes the spin-orbit conserving transitions whereas the difference potential $V^- = \frac{1}{2}(V_{A'} - V_{A''})$ describes the spin-orbit changing transitions.

For pure Hund's case (a) molecules the following symmetry rules can be shown to hold for a given rotational transition $|J\rangle \rightarrow |J'\rangle$:

$$\sigma_{J_e \rightarrow J'_e} = \sigma_{J_f \rightarrow J'_f} \quad (1)$$

and

$$\sigma_{J_e \rightarrow J'_f} = \sigma_{J_f \rightarrow J'_e}, \quad (2)$$

and only differences between symmetry changing and symmetry conserving transitions are to be expected. If the diatom has an intermediate Hund's case character, however, devia-

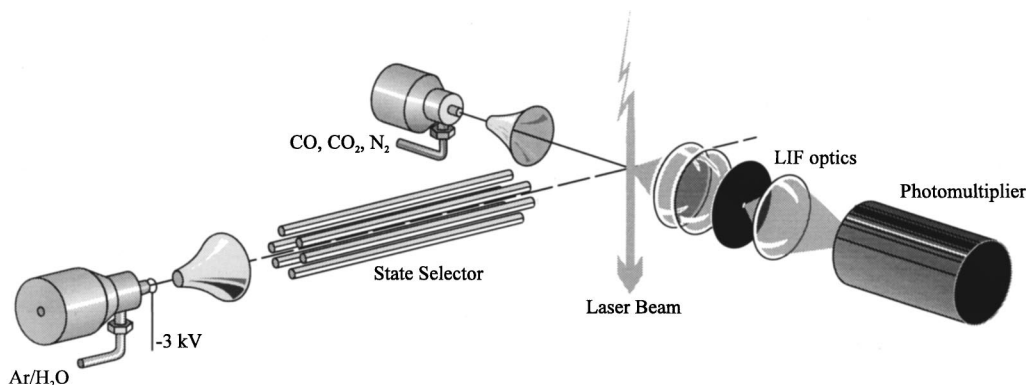


FIG. 1. Artist's impression of the experimental setup.

tions from the symmetry rules are caused by the interference of V^+ and V^- in the matrix elements describing the rotational excitation.

These symmetry considerations can also be used in diatom–diatom scattering calculations if the problem is restricted to planar geometries (i.e., all four atoms have to be in one plane). In the scattering process, however, the out-of-plane configurations may substantially contribute to the cross section. For the scattering of OH by H_2 , for example, the use of out-of-plane configurations for the development of their PES, as done by Offer *et al.*,¹³ gives a better description of the experiment⁷ than the restriction to in-plane configurations as done by Miller and Clary.²²

Kudla *et al.*¹⁸ restricted their calculations on OH–CO to planar geometries. Unlike Alexander they did not calculate the cross sections by using the symmetric and anti-symmetric average of the potentials, but calculated the cross sections for each potential separately. The total cross section for collision induced transitions within the $\Omega = \frac{3}{2}$ manifold was obtained by averaging the two cross sections. Although this method disregards possible interference terms between $V_{A'}$ and $V_{A''}$, it may provide a reasonable description of the collision induced spin–orbit conserving transitions. The calculation of the cross sections for spin–orbit changing transitions, however, cannot be performed this way. Kudla *et al.* also restricted their calculations to collisions of OH and CO molecules in their corresponding rotational ground state. The *ab initio* PES used by Kudla *et al.* was designed to describe inelastic scattering. It contains two potential wells, which correspond to the OH–CO and OH–OC van der Waals complexes. This potential-energy surface, however, is not suitable to describe the formation of the chemically bonded HOCO complex.²³ To investigate the influence of the HOCO complex formation on the inelastic cross sections Kudla *et al.* used a potential-energy surface developed by Schatz *et al.*¹⁹ It was found that for low collisional energies and for excitation to low rotational states, $J = \frac{5}{2}$ or $\frac{7}{2}$, the complex cross section contributes for only a few percent to the total cross section. For excitation to rotational states with $J = \frac{9}{2}$, $\frac{11}{2}$, or $\frac{13}{2}$, however, the complex cross section is calculated to be roughly 40% of the direct cross section (the cross section for scattering processes without complex formation) with a relatively small dependence on the collision energy. As a result one would expect that CO and N_2 behave very differ-

ently in collision induced transitions to states with $J \geq \frac{9}{2}$ due to the large influence of the complex formation.

In the present experiment measurements have been performed on collision induced transitions from the lowest rotational state ($J = \frac{3}{2}$) to states with J up to $\frac{9}{2}$. The obtained rotational state-to-state cross sections are compared with the results obtained by Sonnenfroh *et al.*¹⁷ and Kudla *et al.*¹⁸ With respect to the transitions to $\Pi_{3/2}$, $J = \frac{5}{2}$ and $\Pi_{1/2}$, $J = \frac{1}{2}$ parity propensity rules are found which are obeyed also in collisions of OH with He, Ar, and H_2 .^{2,7}

II. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1 and will only briefly be outlined here. For a more detailed description the reader is referred to previous papers.^{2,7} In the pulsed crossed molecular beam experiment two differentially pumped vacuum chambers are used: One chamber for the production of the primary OH beam, the state selection and the collision process, and the other chamber for the production of the secondary beam (N_2 , CO, and CO_2). During operation the pressure in the collision chamber is approximately 1×10^{-5} mbar.

The primary beam is produced by expanding a 1.6% H_2O in 1.5 bar Ar mixture through a modified Bosch valve. The OH radical is produced in an electrical discharge during this expansion. A 4 mm skimmer separates the expansion region from the electrostatic state selector and serves mainly to prevent most of the ions produced in the discharge from being captured by the selector rods. The state selector consists of a hexapole which focuses OH molecules in the upper $J = \frac{3}{2}$ Λ -doublet state (f symmetry) in the collision area. In order to obtain also data for the molecules in the lower Λ -doublet state (e symmetry), the state selector can be removed. The distance between the focus of the state selector, which coincides with the scattering volume, and the hexapole is ~ 4 cm. When no state selector is used, the valve and skimmer are positioned closer to the scattering region; the distance from the nozzle to the scattering region is then ~ 6 cm. The secondary beam is also produced using a modified Bosch valve. The initial rotational state distribution of the secondary beam has not been determined, but it can be expected that not all molecules are in their rotational ground state, because the cooling is not perfect. The average velocities of the different secondary beam molecules were deter-

mined by placing a fast ionization gauge on the beam axis and measuring the arrival time for different distances between the nozzle and the gauge.

The OH state detection after scattering is done by LIF in the 308 nm region via the $A^2\Sigma_{1/2}^-, v'=0 \leftarrow X^2\Pi_{3/2}, v''=0$ transition, using a frequency doubled dye laser which is pumped by an excimer laser and a UG11 filter to block stray light. The light is collected by optics and detected by a photomultiplier tube. The photomultiplier signal is integrated on a boxcar and subsequently digitized on a shot-to-shot basis and stored in a computer. The averaged output of the boxcar is used as a monitor via a chart recorder.

Measurements of the collision induced population distribution have been performed up to rotational states with $J=\frac{9}{2}$ for the $\Omega=\frac{3}{2}$ states and up to $J=\frac{5}{2}$ for collision induced transitions to the $\Omega=\frac{1}{2}$ manifold. The upper Λ -doublet states (with f -symmetry) are probed by Q_1 and P_2 transitions, whereas the population of the lower Λ -doublet states is measured by Q_2 and P_1 transitions. Because the $Q_2(2)$ and the $Q_2(3)$ lines coincide within the linewidth of the laser (0.15 cm^{-1}) the $\Omega=\frac{1}{2}, J=\frac{3}{2}, e$ and $\Omega=\frac{1}{2}, J=\frac{5}{2}, e$ states cannot be probed separately. It is important to keep in mind that both states are probed in one single measurement, even if only is referred to the $\frac{1}{2}, \frac{5}{2}, e$ state. In one measurement session the population of each final state is probed separately, a thousand times with and one thousand times without collisions, with the laser kept at a fixed frequency on top of the line. Four to six measurement sessions per scattering partner were performed with and without a state selector.

III. DATA REDUCTION

The population of an excited OH state $|k\rangle$ is probed with and without collisions. Subtraction of the results yields the scattering signal δS_k , which is the difference in total fluorescence with and without collisions. The cross section for collision induced excitation from an initial state $|i\rangle$ to the state $|k\rangle$ can be deduced (in the case of saturation of the LIF transition) by²

$$\sigma_{i \rightarrow k} \propto \frac{\delta S_k}{n_i F}, \quad (3)$$

where n_i is the population of the initial state before collisions take place and F the flux-density transformation. This factor comes into account because the cross section depends on the flux of the molecules, while LIF probes the density of the molecules. It can be shown that for our experimental conditions F is nearly the same for all final states $|k\rangle$.² As a result the total cross section $\sigma_{i \rightarrow k}$ is directly proportional to the scattering signal δS_k . When the state selector is used the relative cross sections for transitions from the $\frac{3}{2}, \frac{3}{2}, f$ state are obtained ($\sigma_{f \rightarrow k}$) from δS_k for all states up to $\Omega=\frac{3}{2}, J=\frac{9}{2}, \epsilon$ and $\Omega=\frac{1}{2}, J=\frac{5}{2}, \epsilon$, with ϵ either e or f . When no hexapole is used, the sum of the relative cross sections $\sigma_{3/2, f \rightarrow J, \epsilon} + 0.68\sigma_{3/2, e \rightarrow J, \epsilon}$ is obtained. The factor 0.68 shows up because the $\frac{3}{2}, \frac{3}{2}, e$ state contains 68% of the population of the $\frac{3}{2}, \frac{3}{2}, f$ state. As a consequence the results can not simply be subtracted to yield the cross section $\sigma_{3/2, e \rightarrow J, \epsilon}$, but have to be scaled first. Using the scaling method described by Schreel and Ter Meulen⁷ the cross sections for transitions from the $\frac{3}{2}, \frac{3}{2}, e$ state are obtained.

The initial state preparation is not perfect. With the hexapole switched on 93.5% of the OH molecules in the collision area is in the upper $J=\frac{3}{2}$ Λ -doublet state and 6.5% is in the upper $J=\frac{5}{2}$ state. Consequently, instead of a pure cross section for the $|i\rangle \rightarrow |k\rangle$ transition rather a sum of two cross sections is obtained. The contribution of the $J=\frac{5}{2}$ state is generally small, but can be significant for excitation to states which are weakly coupled to the $J=\frac{3}{2}$ state.² The measured cross sections, however, will be labeled by the initial $J=\frac{3}{2}$ Λ -doublet state and the final state, because this gives by far the largest contribution to the cross section. When comparing the measured results with theory, the contribution of the $J=\frac{5}{2}$ molecules is taken into account on the basis of the measured population distribution. This holds for the measurements without hexapole as well.

Since the density distribution of the secondary beam in the collision region is not exactly known, it is not possible to determine quantitative cross sections. When calculations would be available, the sum of all measured relative cross sections (both from the $\frac{3}{2}, \frac{3}{2}, f$ as well as from the $\frac{3}{2}, \frac{3}{2}, e$ state) could be scaled to the sum of all calculated cross sections, yielding absolute state-to-state cross sections, as was done for He, Ar, and H₂ by Schreel *et al.*^{2,7} No calculations of Λ -doublet resolved cross sections for N₂, CO, and CO₂ have been reported, and only relative cross sections can be derived from the measurements. It is, however, possible to compare the cross sections for CO, N₂, and CO₂. To do this, the expression for the absolute scattering signal has to be considered

$$S_k = C \int_{\text{coll. area}} \sigma_{i \rightarrow k} v_{\text{rel}}(x) n_{\text{sec}}(x) n_{\text{OH}}(x) dx, \quad (4)$$

where C is a constant related to the LIF detection efficiency, $v_{\text{rel}}(x)$ is the relative velocity between both collision partners, $n_{\text{sec}}(x)$ the density of the secondary beam, and $n_{\text{OH}}(x)$ the density of OH molecules in the collision area. The integration has to be performed over the whole collision area. However, since the masses of the collision partners are not much different, it seems a reasonable assumption that the flow pattern, and hence, also the spatial dependence of the density is the same for all three scatterers. As a result one may omit the integral when comparing the cross sections for CO, N₂, and CO₂. Approximating $v_{\text{rel}}(x)$ by the average relative velocity and omitting $n_{\text{OH}}(x)$ because it is the same for all three collision partners, the relative cross sections can be compared to each other by dividing the measured scattering signal by $v_{\text{rel}} \cdot n_{\text{sec}}$. The secondary beam density is not known, but is estimated to be linearly proportional to the backing pressure of the secondary beam valve. Since the backing pressure of the secondary valve is always adjusted to obtain a 10% decrease of the $Q_1(1)$ transition (to fulfill the single collision condition), the relation between the secondary beam densities follows:

$$\begin{aligned} \left(\sum_k \sigma_{i \rightarrow k} v_{\text{rel}} n_{\text{sec}} \right)_{\text{N}_2} &= \left(\sum_k \sigma_{i \rightarrow k} v_{\text{rel}} n_{\text{sec}} \right)_{\text{CO}} \\ &= \left(\sum_k \sigma_{i \rightarrow k} v_{\text{rel}} n_{\text{sec}} \right)_{\text{CO}_2}. \end{aligned} \quad (5)$$

TABLE I. Experimental relative state-to-state cross sections of OH in collisions with N_2 , CO, and CO_2 . The cross sections are scaled to each other, as described in Sec. III.

Final state			Initial state: $3/2, 3/2, f$		
			N_2	CO	CO_2
Ω	J	ϵ	$E_{\text{coll}}=410 \text{ cm}^{-1}$	450 cm^{-1}	400 cm^{-1}
3/2	5/2	<i>f</i>	2.7 ± 0.3	5.4 ± 0.3	2.3 ± 0.3
	7/2	<i>f</i>	0.99 ± 0.08	1.63 ± 0.10	2.01 ± 0.08
	9/2	<i>f</i>	0.09 ± 0.01	0.16 ± 0.05	0.23 ± 0.05
	3/2	<i>e</i>	37.3 ± 0.4	44.7 ± 0.5	51.4 ± 0.6
	5/2	<i>e</i>	5.47 ± 0.08	5.54 ± 0.12	6.11 ± 0.09
	7/2	<i>e</i>	0.88 ± 0.04	1.27 ± 0.06	1.47 ± 0.04
1/2	9/2	<i>e</i>	0.33 ± 0.07	0.08 ± 0.03	0.23 ± 0.03
	1/2	<i>f</i>	1.39 ± 0.09	1.65 ± 0.10	1.17 ± 0.06
	3/2	<i>f</i>	0.52 ± 0.07	0.64 ± 0.08	0.54 ± 0.05
5/2	<i>f</i>	0.09 ± 0.04	0.48 ± 0.05	0.21 ± 0.04	
	<i>e</i>	2.0 ± 0.3	1.98 ± 0.06	2.08 ± 0.04	
3/2	<i>e</i>	0.93 ± 0.05	1.37 ± 0.06	1.55 ± 0.05	
Final state			Initial state: $3/2, 3/2, e$		
			N_2	CO	CO_2
3/2	3/2	<i>f</i>	37.3 ± 0.4	44.7 ± 0.5	51.4 ± 0.6
	5/2	<i>f</i>	9.2 ± 0.9	4.7 ± 1.0	8.7 ± 1.1
	7/2	<i>f</i>	1.9 ± 0.3	1.4 ± 0.4	3.0 ± 0.5
	9/2	<i>f</i>	0.27 ± 0.12	0.43 ± 0.08	0.59 ± 0.10
	5/2	<i>e</i>	3.5 ± 0.7	3.5 ± 0.9	0.7 ± 0.7
	7/2	<i>e</i>	2.2 ± 0.3	1.7 ± 0.3	2.2 ± 0.4
1/2	9/2	<i>e</i>	0.83 ± 0.16	0.46 ± 0.07	0.27 ± 0.06
	1/2	<i>f</i>	1.2 ± 0.3	2.2 ± 0.4	2.5 ± 0.4
	3/2	<i>f</i>	0.70 ± 0.15	1.45 ± 0.30	0.81 ± 0.14
5/2	<i>f</i>	0.31 ± 0.10	0.18 ± 0.09	0.47 ± 0.08	
1/2	<i>e</i>	1.2 ± 0.4	1.7 ± 0.4	0.9 ± 0.3	
3/2	<i>e</i>	2.1 ± 0.3	0.8 ± 0.3	1.1 ± 0.3	

Only the cross sections for excitation out of the $\frac{3}{2}, \frac{3}{2}, f$ state are needed to scale the cross sections and the summation ranges over all states which can be excited.

The results are scaled to each other using this equation, but also to our previous values on H_2 . Although this is not the ideal scattering partner to compare to (because the density distribution will be different), it is the only one for which we have data available with the same nozzle diameter and for which accurate scaling to theoretical values is possible. In this way a good estimate of the absolute values is

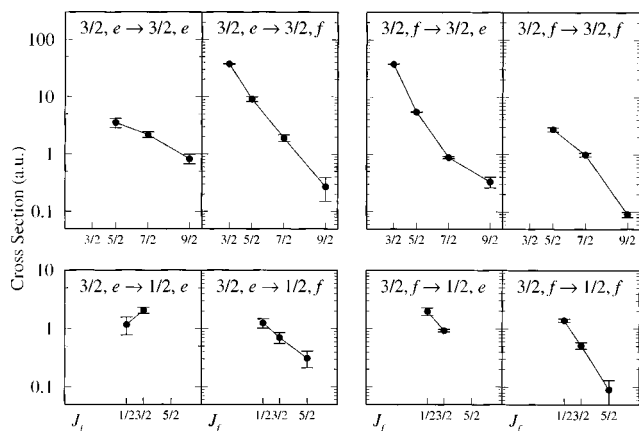


FIG. 2. Relative state-to-state cross sections for rotational excitation of OH in collisions with N_2 at an energy of 410 cm^{-1} .

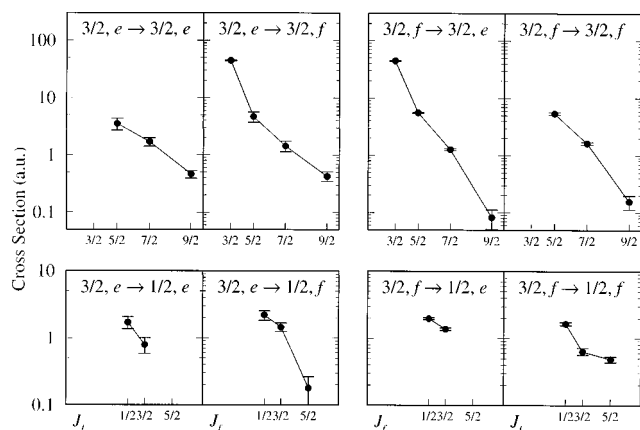


FIG. 3. Relative state-to-state cross sections for rotational excitation of OH in collisions with CO at an energy of 450 cm^{-1} .

obtained. It should be stressed, however, that the results presented in the next section are reliable only with respect to their relative values.

IV. RESULTS AND DISCUSSION

A. State-to-state cross sections

The obtained results for the relative cross sections are presented in Table I and in Figs. 2–4. The collision energy (410 cm^{-1} for N_2 , 450 cm^{-1} for CO and 400 cm^{-1} for CO_2) is the total kinetic energy in the center-of-mass system, as calculated from the measured velocities. When compared to scattering by the light particles He and H_2 ,^{2,7} the most striking feature of the OH– N_2 , OH–CO, and OH– CO_2 collisions is the dominating “energy gap law” dependence of the cross sections, particularly for the spin–orbit conserving transitions. The Λ -doublet cross section, $\sigma_{3/2,f \rightarrow 3/2,e}$ in which only the orientation of the unpaired electron orbital is changed and no rotational excitation takes place, is much larger than the cross sections for the rotational transitions, as can be expected in view of the small Λ -doublet energy splitting. This has also been found for collisions with Ar.² In collisions with He, however, the Λ -doublet cross section is almost zero.² For $n-H_2$ this cross section is definitely not zero, but

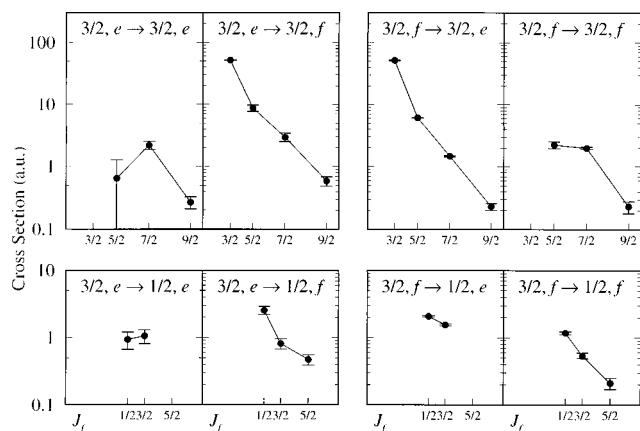


FIG. 4. Relative state-to-state cross sections for rotational excitation of OH in collisions with CO_2 at an energy of 400 cm^{-1} .

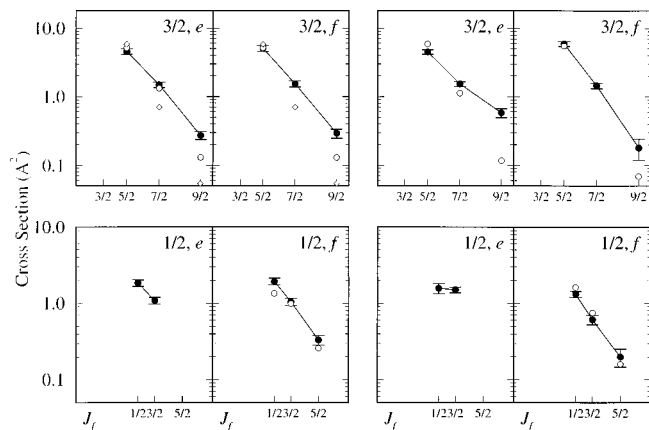


FIG. 5. Comparison between our results (●), the data obtained by Sonnenfroh *et al.* (Ref. 17) (○) and the theoretical results of Kudla *et al.* (Ref. 18) (◇) for the symmetry averaged cross section $\sigma_{e \rightarrow k} + \sigma_{f \rightarrow k}$ for collisions of OH with CO (left; $E_{\text{coll}} = 450 \text{ cm}^{-1}$) and N_2 (right; $E_{\text{coll}} = 410 \text{ cm}^{-1}$) in the upper part the cross sections for transitions to the $\Omega = \frac{3}{2}$, e and f states are given, whereas in the lower part the cross sections for the multiplet changing transitions are shown.

from a comparison with $p\text{-H}_2$ and rotationally “hot” $n\text{-H}_2$ Schreel *et al.*⁷ concluded that this cross section is due to $\text{H}_2(J \neq 0)$ molecules and that the Λ -doublet cross section in collisions with $\text{H}_2(J = 0)$ is small.

One might perhaps conclude that the relative size of the Λ -doublet cross section is determined by the velocity of the collision partner. For light molecules the velocity is high and the collision is described by a sudden approach, in which the electron orbital distribution tends to change its orientation only if simultaneously the molecular rotation is changed. For heavy molecules the velocity is low, and an adiabatic description is more appropriate, where the electron distribution can adapt its orientation without a change of the nuclear rotation. This kinetic picture can be tested by varying the relative velocity, which, in the present experimental setup could be performed by changing the carrier gas of the primary beam. According to Esposti *et al.*,¹² the difference in Λ -doublet cross section for Ar and He is probably due to a combined effect of strongly different velocities and the more attractive potential of OH–Ar.

The most eye catching deviation from the energy gap law is the small cross section for the symmetry conserving transitions $\frac{3}{2}, \frac{3}{2} \rightarrow \frac{3}{2}, \frac{5}{2}$ induced in collisions with CO_2 . Also the cross sections for excitation to the $\Omega = \frac{1}{2}$ states do not obey an energy gap law for all scattering partners. Some more deviations from the energy gap law will come to light when a detailed look is taken at the symmetry of the initial and final state. First, however, the symmetry averaged cross sections will be discussed.

B. Symmetry averaged cross sections

In Fig. 5 the symmetry averaged cross sections $\frac{1}{2}(\sigma_{3/2,e \rightarrow J,\epsilon} + \sigma_{3/2,f \rightarrow J,\epsilon})$ are compared to the results of Sonnenfroh *et al.*¹⁷ In their experiment on OH in collisions with CO and N_2 over 98% of the OH molecules is initially in one of both $\frac{3}{2}, \frac{3}{2}$ Λ -doublet states, which are equally populated.

Because no state selector was used, they were unable to measure the cross sections $\sigma_{3/2,e \rightarrow J,\epsilon}$ and $\sigma_{3/2,f \rightarrow J,\epsilon}$ separately, and hence their results are symmetry averaged. For all $\Omega = \frac{3}{2}$ manifold components up to $J = \frac{11}{2}$ (except for the $J = \frac{7}{2}$ state, which they cannot resolve) and up to $J = \frac{7}{2}$ in the $\Omega = \frac{1}{2}$ manifold (only f states, because of the spectral congestion in the Q_2 -branch) the cross sections were measured as a function of the collision energy. They found little difference between the OH– N_2 and OH–CO systems. For N_2 induced transitions to high rotational states ($J \geq \frac{9}{2}$) in the $\Omega = \frac{3}{2}$ manifold they did, however, observe a preference for excitation to the e -states over the f -states. For collisions with CO such a preference was not observed. In order to compare the results of Sonnenfroh *et al.* with our results (Fig. 5), the sum of all cross sections reported in Ref. 17 at an energy of 450 cm^{-1} , was set equal to the sum of our measured cross sections. It should be noted that in the paper of Sonnenfroh *et al.* no experimental accuracies are given. In Fig. 5 our results on collision induced transitions to the $\Omega = \frac{3}{2}$ states are also compared with the theoretical values of Kudla *et al.*¹⁸ for OH–CO collisions at a collision energy of 375 cm^{-1} . They have calculated the cross sections for excitation to $|e\rangle$ states only and postulated that the cross sections to $|f\rangle$ states would be the same. In this graph the values obtained by Sonnenfroh *et al.*¹⁷ and the theoretical values of Kudla *et al.* are scaled to the present experimental values for transitions to $\Omega = \frac{3}{2}$ states, according to

$$\begin{aligned} & \sum_J [\sigma_{3/2,e \rightarrow J,\epsilon} + \sigma_{3/2,e \rightarrow J,f} + \sigma_{3/2,f \rightarrow J,\epsilon} + \sigma_{3/2,f \rightarrow J,f}] \\ & = 2\alpha \sum_J [Q_{A'}(\frac{3}{2} \rightarrow J) + Q_{A''}(\frac{3}{2} \rightarrow J)], \end{aligned} \quad (6)$$

where α is the scaling factor and $Q_{A'}(\frac{3}{2} \rightarrow J)$ and $Q_{A''}(\frac{3}{2} \rightarrow J)$ are the calculated symmetry averaged cross sections by Kudla *et al.*

In general, both experiments are in relatively good agreement with each other and with theory. Especially this agreement with theory is somewhat surprising, because Kudla *et al.* only took OH($J = \frac{3}{2}$)–CO($J = 0$) into account, while in the experiments a significant fraction of the CO molecules will be in rotationally excited states. Apparently the rotational state of CO has a limited influence on the rotational dependence of the cross sections. When compared to the results of Sonnenfroh *et al.*¹⁷ and the theoretical values,¹⁸ our cross sections are smaller for excitation to the $\frac{3}{2}, \frac{5}{2}$ states and larger for transitions to higher J states. The cross sections obtained by Sonnenfroh *et al.* lay in between the present values and the theoretical results. This is probably due to a relatively high rotational temperature of the primary beam in our experiment, a lower temperature in the experiment by Sonnenfroh *et al.* and an ideal temperature of zero degrees in the calculations. A higher rotational temperature would mean that more OH molecules are in the $\frac{3}{2}, \frac{5}{2}$ states. As a result the measured net cross section to the $\frac{3}{2}, \frac{5}{2}$ states is reduced, because molecules are also scattered out of the $\frac{5}{2}$ states. And the cross sections for transitions to higher states will be enlarged because the energy gap for excitation

out of the $\frac{3}{2}, \frac{5}{2}$ states is smaller than for excitation out of the $\frac{3}{2}, \frac{3}{2}$ states.

Without state selection both $\frac{3}{2}, \frac{5}{2}$ states contain roughly 2% of the total OH population and both $\frac{3}{2}, \frac{3}{2}$ states about 48%. In the various collision experiments, the backing pressure of the secondary beam is adjusted, such that a 10% decrease of the $Q_1(1)$ transition is measured. This means that 10% of the OH molecules in the $\frac{3}{2}, \frac{3}{2}, f$ state is scattered to other states. In collisions with CO and N₂, about 8% of these molecules make a transition to the $\frac{3}{2}, \frac{5}{2}, f$ state. As a result $\sim 1.6\%$ of all OH molecules is scattered from one of the $\frac{3}{2}, \frac{3}{2}$ Λ -doublet states into the $\frac{3}{2}, \frac{5}{2}, f$ state. Assuming that 10% of the molecules which are initially in the $\frac{3}{2}, \frac{5}{2}, f$ state are scattered out of this state, one will measure the population of the $\frac{3}{2}, \frac{5}{2}$ state, with and without collisions to be: $1.8 + 1.6 = 3.4\%$ and 2.0% , respectively. Instead of a population transfer of 1.6% from the $\frac{3}{2}, \frac{3}{2}, f$ to the $\frac{3}{2}, \frac{5}{2}, f$ state we measure a population transfer of 1.4% . Hence the measured cross section is 12.5% too small. When comparing the present results with the results obtained by Kudla *et al.* and Sonnenfroh *et al.* our cross sections for excitation to the $\frac{3}{2}, \frac{3}{2}, f$ state are 88% of the cross sections obtained by Kudla and Sonnenfroh, which is in good agreement with our explanation based on the initial population of the $\frac{3}{2}, \frac{5}{2}$ state.

For the symmetry averaged cross sections for OH–N₂ some symmetry propensities are observed. There is a preference for f -symmetry over e -symmetry in the excitation to the $\frac{3}{2}, \frac{5}{2}$ state and a preference for e -symmetry over f -symmetry in the excitation to the $\frac{3}{2}, \frac{9}{2}$ and $\frac{1}{2}, \frac{3}{2}$ Λ -doublet states. No propensities are observed for the symmetry averaged cross sections for OH–CO. The symmetry propensity for $\frac{3}{2}, \frac{5}{2}, f$ in collisions with N₂ has not been observed by Sonnenfroh *et al.*¹⁷ In order to carefully check the experimental accuracy, six measurement series, with and without state selector, were performed on the cross sections to the $\frac{3}{2}, \frac{5}{2}, e$ states. All measurements show a good statistical behavior. The deviation cannot be explained by the initial difference in population between the $\frac{3}{2}, \frac{5}{2}$ Λ -doublet states. The measured initial relative population difference is the same as the relative difference in population of the $\frac{3}{2}, \frac{3}{2}$ states. Hence after scaling (in order to obtain the cross sections for transitions from the $\frac{3}{2}, \frac{3}{2}, e$ state, see Sec. III) the population of the $\frac{3}{2}, \frac{5}{2}, e$ and $\frac{3}{2}, \frac{5}{2}, f$ states will be equal. Moreover, the same initial population effects would be expected for the different scattering partners. For CO a good agreement with Sonnenfroh's values is obtained, which supports the assumption that these effects are negligible. It should be mentioned that for vibrationally excited OH colliding with N₂, Crosley measured a propensity for final f symmetry in excitation to the $\frac{3}{2}, \frac{5}{2}$ state as well.²⁰ The preference for population of the $\frac{3}{2}, \frac{9}{2}, e$ state in collisions with N₂ was also reported by Sonnenfroh *et al.* More general, they also observed a preference for e -symmetry in spin–orbit conserving transitions to higher J -states. These states are energetically not accessible at our collisional energy. The fact that this propensity is not observed for OH–CO may be explained by the role of HOCO complex formation.¹⁸

Remarkable is the relatively large value for the sum of the symmetry averaged cross sections for transitions to the

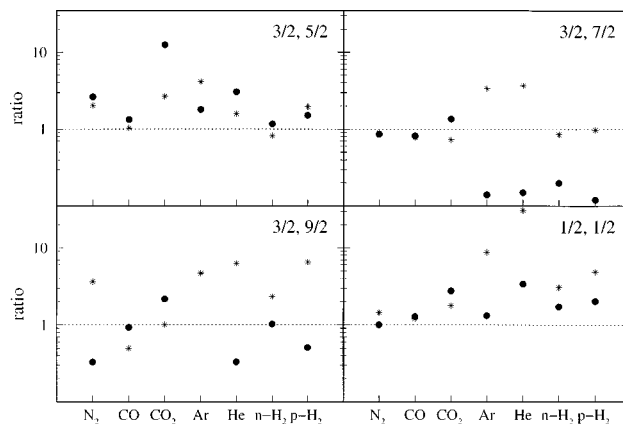


FIG. 6. Ratio of cross sections for symmetry changing transitions and symmetry conserving transitions. The asterisks are for $\sigma_{3/2, f \rightarrow J, f} / \sigma_{3/2, f \rightarrow J, f}$ and the circles for $\sigma_{3/2, e \rightarrow J, f} / \sigma_{3/2, e \rightarrow J, e}$. The initial state is the $\Omega = \frac{3}{2}, J = \frac{5}{2}$ state, the Ω and J of the final state is indicated in the upper right corner of each graph.

$\frac{1}{2}, \frac{3}{2}, e$ and $\frac{1}{2}, \frac{5}{2}, e$ states in collisions with N₂ (plotted as a single point in Fig. 5 since the states cannot be probed separately) when compared to the sum of the cross sections for transitions to the corresponding f states. This preference has not been observed by Sonnenfroh *et al.* because they have not measured the cross section for the transition to the $\frac{1}{2}, J, e$ states.

C. Symmetry effects

Detailed information on symmetry propensities is obtained from the Λ -doublet resolved state-to-state cross sections. In Fig. 6 the preferences for symmetry changing over symmetry conserving transitions, $\sigma_{3/2, e \rightarrow J, f} / \sigma_{3/2, e \rightarrow J, e}$ and $\sigma_{3/2, f \rightarrow J, e} / \sigma_{3/2, f \rightarrow J, f}$, are plotted for the different scattering gases considered, including He, Ar, and H₂. For collisional excitation to the $\frac{3}{2}, \frac{5}{2}$ Λ -doublet states the symmetry changing transitions are preferred above symmetry conserving transitions for all molecules except n -H₂. This effect is especially very large in collisions with He, Ar, and CO₂, but very small for OH–CO collisions. For collisional excitation to the higher J states in the $\Pi_{3/2}$ manifold no general propensity is observed.

For spin–orbit changing transitions to the $\Omega = \frac{1}{2}$ manifold, symmetry changing transitions are preferred in transitions to the $J = \frac{1}{2}$ states for all scattering gases. This preference is remarkably large in collisions with He. For transitions to the $\frac{1}{2}, \frac{3}{2}$ states no general conclusions can be made, also because the $\frac{1}{2}, \frac{3}{2}$ and $\frac{1}{2}, \frac{5}{2}$ states cannot be probed separately. It should be noted that for CO the symmetry effects are marginal. Obviously OH–CO is the most “classical” system of all systems considered. When considering parity instead of symmetry it turns out that conservation of parity is preferred in the transitions to $\frac{3}{2}, \frac{5}{2}$ and $\frac{1}{2}, \frac{1}{2}$. A similar parity propensity has been observed by Crosley for spin–orbit changing collisions of OH with He.²⁴

It can be concluded that in spin–orbit conserving transitions to the $J = \frac{5}{2}$ state the orientation of the unpaired electron

lobe is preferably changed, whereas the reverse is true for the spin-orbit changing transitions to the $J=\frac{1}{2}$ state.

D. Comparison between OH-CO, OH-N₂, and OH-CO₂

As explained before the potential-energy surfaces describing OH-CO and OH-N₂ collisions are very different. The long-range potential for HO-CO is dominated by the dipole-dipole interaction whereas the long-range potential for OH-N₂ is mainly determined by the dipole-quadrupole interaction. Furthermore, the short-range potential for OH-CO has two small OH-CO and OH-OC van der Waals wells and one deep HOCO complex well, while the potential for OH-N₂ is mainly repulsive. Hence, it is surprising to see that the state-to-state cross sections for both collision partners are nearly the same, except for the cross sections to the $\frac{3}{2}, \frac{5}{2}$ states, which deviate significantly. A possible explanation is that the rotational temperature of the secondary beam is so high that it contains a large amount of rotationally excited molecules. As a result most anisotropic effects would be smeared out, reducing the differences between the potentials for CO and N₂. This could be checked by lowering the temperature of the secondary beam source, but this is at present not possible with our setup.

One would expect that these outsmearing effects would be larger for heavier collision partners since higher rotational states are populated due to a smaller B constant. On the other hand the average rotational energy may be smaller as a result of a stronger rotational cooling in the expansion. This might be the case for collisions between OH and CO₂. Compared to OH-N₂ and OH-CO there are large differences between the cross sections to the $\frac{3}{2}, \frac{5}{2}, e$ and $\frac{3}{2}, \frac{5}{2}, f$ states and similarly to the $\frac{1}{2}, \frac{1}{2}, e$ and $\frac{1}{2}, \frac{1}{2}, f$ states. Unfortunately, no calculations or other measurements on OH-CO₂ collisions are available to compare our results with.

The total inelastic cross sections for all three scattering partners vary in a way which can be understood from simple arguments. With the scaling applied as described in Sec. III, the total relative inelastic cross sections for scattering from the $\frac{3}{2}, \frac{3}{2}, f$ state for N₂, CO, and CO₂ are 52.7, 66.5, and 69.3, respectively. When only the physical size of the molecules is taken into account, one would expect that in the case of CO₂ the total cross section is the largest. This is also what is observed. The difference between N₂ and CO can be understood in terms of the type of interaction potential. The dipole-dipole coupling in the case of CO gives rise to a longer range interaction potential and hence a larger total cross section.

V. CONCLUSION

We have obtained Λ -doublet resolved state-to-state cross sections for rotational excitation of OH in collisions with CO, N₂, and CO₂. In general the results can be described by a classical energy gap law, but strong deviations are observed which are ascribed to quantum-mechanical interferences. Possibly these quantum-mechanical effects are partially smeared out by the rotation of the molecules in the secondary beam. This could be checked by lowering the rotational temperature of the collision partner.

Apart from excitation to the $\frac{3}{2}, \frac{5}{2}$ states in collisions with N₂, there is no significant preference for excitation to either the e or f Λ -doublet states when averaged over the cross sections for both $J=\frac{3}{2}$ Λ -doublet states, but there are preferences with respect to symmetry changing or conserving transitions. In collision induced transitions to the $\frac{3}{2}, \frac{5}{2}$ states symmetry changing transitions are preferred above symmetry conserving transitions. This propensity is observed also for previously studied collision partners (Ar, He, p -H₂). Symmetry changing is also preferred in transitions to the $\frac{1}{2}, \frac{1}{2}$ states, for all collision partners studied. For both transitions the change of symmetry corresponds to a conservation of parity. For collision induced transitions to higher J values in the $\Omega=\frac{3}{2}$ as well as in the $\Omega=\frac{1}{2}$ manifold no general propensity rules can be deduced.

The present symmetry averaged results on OH-CO and OH-N₂ agree with the results obtained by Sonnenfroh *et al.*¹⁷ and the calculations of Kudla *et al.*¹⁸ The small differences are probably due to a higher rotational temperature of the primary beam in our experiment. Only the discrepancy in cross sections to the $\frac{3}{2}, \frac{5}{2}$ states in OH-N₂ collisions cannot be explained.

No systematic differences between OH-CO and OH-N₂ have been measured. This can be explained if the expected HOCO complex formation is not important for excitations to rotational states up to $J=\frac{9}{2}$, if the PES is smeared out by rotation of the molecules in the secondary beam or if the differences in the PES just do not lead to differences in the cross section.

It is remarkable that the OH-CO system shows the most classical behavior of all systems considered. This role was expected to be played by OH-CO₂ as a result of the larger number of rotational states involved in the collision process. It turns out, however, that, compared to OH-CO and OH-N₂, this system shows the largest symmetry effects which probably are due to quantum interference terms. Possibly the average rotational energy of CO₂ is smaller due to a better rotational cooling in the expansion. Further conclusions have to await detailed experiments with a full characterization of the rotational population distribution of the collision partners.

¹R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University Press, New York, 1987).

²K. Schreel, J. Schleipen, A. Eppink, and J. J. ter Meulen, *J. Chem. Phys.* **99**, 8713 (1993).

³R. G. Macdonald and K. Liu, *J. Chem. Phys.* **91**, 821 (1989).

⁴L. S. Botuyan, A. G. Suits, P. L. Houston, and B. J. Whitaker, *J. Chem. Phys.* **97**, 6342 (1993).

⁵J. J. van Leuken, F. H. W. van Amerom, J. Bulthuis, J. G. Snijders, and S. Stolte, *J. Chem. Phys.* **99**, 15573 (1995).

⁶D. G. Sauder, D. Patel-Misra, and P. J. Dagdigian, *J. Chem. Phys.* **91**, 5316 (1989).

⁷K. Schreel and J. J. ter Meulen, *J. Chem. Phys.* **105**, 4522 (1996).

⁸P. Andresen, N. Aristov, V. Beushausen, D. Häusler, and H. W. Lülf, *J. Chem. Phys.* **95**, 5763 (1991).

⁹R. G. Macdonald and K. Liu, *J. Chem. Phys.* **93**, 2443 (1990).

¹⁰P. J. Dagdigian, in *The Chemical Dynamics and Kinetics of Small Radicals*, edited by K. Liu and A. Wagner (World Scientific, Singapore, 1995).

¹¹J. C. Whitehead, *Rep. Prog. Phys.* **59**, 993 (1996).

- ¹²A. D. Esposti, A. Berning, and H.-J. Werner, *J. Chem. Phys.* **103**, 2067 (1995).
- ¹³A. R. Offer, M. C. van Hemert, and E. F. van Dishoeck, *J. Chem. Phys.* **100**, 362 (1994).
- ¹⁴J. Warnatz, U. Maas, and R. W. Dibble, *Combustion* (Springer Verlag, Berlin, 1996).
- ¹⁵E. W. Rothe, Y. W. Gu, and G. P. Reck, *Appl. Opt.* **35**, 934 (1996).
- ¹⁶R. P. Wayne, *Chemistry of Atmospheres*, 2nd ed. (Clarendon, Oxford, 1991).
- ¹⁷D. M. Sonnenfroh, R. G. Macdonald, and K. Liu, *J. Chem. Phys.* **94**, 6508 (1991).
- ¹⁸K. Kudla, A. G. Koures, L. B. Harding, and G. C. Schatz, *J. Chem. Phys.* **96**, 7465 (1992).
- ¹⁹G. C. Schatz, M. S. Fitzcharles, and L. B. Harding, *Faraday Discuss. Chem. Soc.* **84**, 359 (1987).
- ²⁰D. Crosley (private communication).
- ²¹M. H. Alexander, *J. Chem. Phys.* **92**, 337 (1985).
- ²²S. M. Miller and D. C. Clary, *J. Chem. Phys.* **98**, 1843 (1993).
- ²³M. Aoyagi and S. Kato, *J. Chem. Phys.* **88**, 6409 (1988).
- ²⁴I. J. Wysong, J. B. Jeffries, and D. R. Crosley, *J. Chem. Phys.* **94**, 7547 (1991).