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Close coupling results for inelastic collisions of NH₃ and Ar. A stringent test of a spectroscopic potential

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Abstract

We have calculated state-to-state total cross sections for rotational excitation and inversion of NH₃ by collisions with Ar using the close coupling method. The Ar–NH₃ interaction potential has been obtained from a fit to the spectrum of this van der Waals molecule. The calculated cross sections agree to within about 30% with the measured values; the estimated error in the latter is 10% to 20%.

1. Introduction

The quality of an intermolecular potential energy surface can be assessed by comparing the experimentally determined spectrum of the dimer – a bound van der Waals complex – with a theoretical spectrum, which is computed from the given potential. Since it is currently possible to obtain accurate state-to-state total and differential cross sections, both experimentally and computationally, one can use scattering data as a further test of the potential surface. The latter approach is complementary to the former, as scattering states and bound states probe the intermolecular potential surface in different regions.

In this Letter, we investigate to what extent an empirical potential that is principally derived from bound states information (far-infrared vibration–rotation–tunneling spectra), is capable of reproducing

scattering data. This constitutes a stringent test of such a potential. To this end we performed close coupling calculations to describe collisions of NH₃ with Ar, making use of a potential that was determined from a parametrized model potential by optimizing the parameters in a fit of the spectrum [1]. We computed state-to-state total cross sections for collision-induced transitions between rotation-inversion (j_k^\pm) states of NH₃ and compare these with experimental values [2].

In an earlier paper [3], we performed identical calculations using the ab initio potential described in Ref. [4] and a second potential, in which the original ab initio potential contains one scaling parameter that was chosen to improve the agreement with the spectroscopic data [5]. This second potential proved to give better agreement with the measured scattering data as well. We will also compare the cross sections obtained from this scaled ab initio potential with those obtained from the empirical potential.

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2. Intermolecular potentials

The empirical and ab initio potential surfaces are described in Refs. [1,4], respectively. Ref. [1] also contains a brief comparison of the two potentials. Here, we summarize their most important features.

The three-dimensional empirical potential surface has been determined from a least-squares fit to 61 far-infrared and microwave vibration–rotation–tunneling measurements and to temperature-dependent second virial coefficients. A surface with thirteen variable parameters has been optimized to accurately reproduce the spectroscopic observables, using the collocation method [6]. This model surface contains long-range attractive forces of induction and dispersion and short range Coulombic and electron exchange repulsive forces. The long-range dispersion coefficients were taken from ab initio calculations [4,7], since they cannot be properly derived from experiment. The three intermolecular coordinates (R , ϑ , φ) were treated without invoking any approximation regarding their separability.

The ab initio potential has been obtained by Heitler–London short range calculations and from multipole-expanded dispersion and induction long-range contributions. A Tang–Toennies-like damping was applied to the long-range energy. These calculations were made for four different values of the NH_3 umbrella angle ρ , which is defined as the angle between the C_3 axis and one of the N–H bonds. Each surface is given in the form of an expansion in spherical harmonics through $l=7$. The scaling consists in multiplying a short range parameter in one of the expansion coefficients, $v_{33}(R)$, by a factor of 1.43, for all values of the inversion coordinate ρ , which appeared to improve the agreement with the spectrum considerably [5].

The ab initio potential is expressed with respect to a body-fixed coordinate frame in which the z axis coincides with the C_3 axis of ammonia, with the nitrogen atom being on the positive z axis. The frame origin is in the center of mass of NH_3 and one hydrogen nucleus is put into the x – z plane, with positive x . The position vector \mathbf{R} of the Ar atom is given by its usual spherical polar coordinates (R , Θ , Φ). The empirical potential is expressed in a slightly different frame, in that the nitrogen atom is put on the negative z axis. This means that we have to apply the transformation

$\Theta = \pi - \vartheta$ and $\Phi = \varphi$, in order to express both potentials in the same coordinate system.

Another important difference between the two potentials is that the ab initio potential depends on ρ , enabling us to take the inversion coordinate explicitly into account in the scattering calculations, whereas the empirical potential does not. This implies that for this potential we have to apply the delta function model to treat the NH_3 inversion motion. It has been shown [3], however, that this has only a small effect – in the order of 3% – on the cross sections as compared to calculations that do take the inversion coordinate explicitly into account. It therefore does not impede a meaningful comparison.

3. Computational aspects

The close coupling calculations were carried out with the HIBRIDON inelastic scattering code². A detailed discussion of the parameters used in the calculations, and their settings, can be found in Ref. [3]. Again, we restrict ourselves to giving only the essentials.

The values of the total energies are determined by the two experimental relative kinetic energies: 280 and 485 cm^{-1} . The ortho- NH_3 with initial state $j=k=0$ has zero internal energy, so the total energies are equal to the relative kinetic energies. The initial $j=k=1$ state of para- NH_3 , which is the ground state of this species, has an internal energy of 16.245 cm^{-1} . The total energies are consequently set equal to 296.245 and 501.245 cm^{-1} . The molecular levels in the angular basis set are retained up to $j=9$ inclusive, with all allowed values of k . This means that for ortho- NH_3 34 levels are included (with a maximum energy of 895 cm^{-1}), 11 of which are asymptotically accessible in the lower, and 19 in the higher energy case. Out of the 66 levels for para- NH_3 (with a maximum energy of 891 cm^{-1}) 24 and 40 levels are accessible, respectively. Since the averaging of the rotational constants over the umbrella inversion wave

² HIBRIDON is a package of programs for the time-independent quantum treatment of inelastic collisions and photodissociation written by M.H. Alexander, D. Manolopoulos, H.-J. Werner and B. Follmeg, with contributions by P.F. Vohralik, G. Corey, B. Johnson, T. Orlikowski and P. Valiron.

functions has a small effect [8], we have taken the same value for both inversion states [9]: $B=9.9402\text{ cm}^{-1}$ and $C=6.3044\text{ cm}^{-1}$.

The calculations took about 9 h for ortho-NH₃-Ar and about 91 h for para-NH₃-Ar on an IBM RS/6000 model 370 workstation.

4. Results and discussion

The results of the calculations reported here are compared with the results of a crossed molecular beam experiment described in Ref. [2]. Only differences in population of a specific rotation-inversion state $|i\rangle \equiv j_k^\xi$ before and after the collision are measured. The signal is proportional to

$$\Delta n(i) = \sum_{j \neq i} [n(j)\sigma(j \rightarrow i) - n(i)\sigma(i \rightarrow j)], \quad (1)$$

where $n(i)$ stands for the initial population of state i and $\Delta n(i)$ for the collision-induced change in that population. If the experiment is to yield pure state-to-state cross sections $\sigma(i \rightarrow j)$, only a single state i must be initially populated. This requirement, however, cannot be completely met. For ortho-NH₃ the initial state consists of 92% 0_0^+ and 8% 1_0^+ and for para-NH₃ of 95% 1_1^- and 5% 1_1^+ . The state-to-state cross sections obtained from the calculations therefore must be put into Eq. (1) in order to enable comparison with the observed quantities. The contributions from the 1_0^+ state of the ortho species and the 1_1^+ state of the para species are taken from the same computations (with the same total energy) as the cross sections from the mainly populated initial states. The internal energies of the 1_1^- and 1_1^+ para states are almost equal, but the 1_0^+ state is higher by 19.88 cm^{-1} than the ground state of the ortho species. Still, the assumption that the corrections can be computed for the same total energies as the main contributions is justified, since the cross sections are just weakly dependent on energy.

Only relative values for the cross sections can be derived from the experiment. To facilitate comparison, the sum of the experimental cross sections over all states is set equal to the sum of the calculated cross sections, corrected for the imperfect initial state preparation. The sum contains only cross sections for excitations to levels j_k^ξ that are experimentally ob-

served. In order to get a single parameter as a measure for the overall agreement between the calculated and experimental cross sections, we define the error Q in the following way:

$$Q = \left(\frac{\sum_i (\sigma_{\text{calc},i} - \sigma_{\text{exp},i})^2}{\sum_i \sigma_{\text{exp},i}^2} \right)^{1/2} 100\%, \quad (2)$$

where $\sigma_{\text{calc},i}$ are the (corrected) calculated cross sections, $\sigma_{\text{exp},i}$ are the experimental cross sections, and the summation runs over all measured states belonging to one energy and one species (i.e. ortho or para). Note that these Q values measure the absolute errors in the cross sections, rather than the relative errors; the latter are dominated by a few of the very small values. In Tables 1 and 2 we have listed both the pure state-to-state cross sections and those that are corrected for the imperfect initial state preparation, together with the experimental cross sections and the Q values. The Q values for the cross sections obtained from the scaled ab initio potential, calculated from

Table 1

State-to-state cross sections $\sigma(0_0^+ \rightarrow j_k^\xi)$ for ortho-NH₃-Ar in Å² obtained from the empirical potential. The relative kinetic energies are as indicated. The cross sections given in parentheses are corrected for the imperfect initial state preparation

j_k^ξ	280 cm ⁻¹		485 cm ⁻¹	
	calc.	exp.	calc.	exp.
1_0^+	10.21(5.94)	5.55	7.39(3.64)	3.65
2_0^+	4.59(5.28)	6.16	4.17(4.71)	4.82
3_0^+	2.14(2.05)	2.01	3.38(3.20)	2.00
4_0^+	0.13(0.19)	0.44	0.07(0.18)	1.46
5_0^+	–	–	0.20(0.20)	–
6_0^+	–	–	0.02(0.02)	0.85
3_3^+	0.22(1.06)	3.15	0.10(0.83)	1.42
3_3^-	13.79(13.24)	11.19	12.46(11.85)	12.03
4_3^-	7.19(6.75)	5.28	8.32(7.78)	4.14
4_3^+	0.09(0.46)	1.19	0.05(0.44)	2.28
5_3^+	0.04(0.06)	–	0.00(0.06)	–
5_3^-	0.30(0.29)	–	1.18(1.16)	–
6_3^-	–	–	0.02(0.03)	–
6_3^+	–	–	0.00(0.00)	–
6_6^-	–	–	0.03(0.07)	–
6_6^+	–	–	0.55(0.53)	–
7_6^+	–	–	0.13(0.13)	–
7_6^-	–	–	0.00(0.01)	–
Q^a	23%		31%	

^a For the cross sections from the scaled ab initio potential [3] these errors are 54% and 55%, respectively.

Table 2
State-to-state cross sections $\sigma(1_{\bar{1}} \rightarrow j_k^{\epsilon})$ for para-NH₃-Ar in Å² obtained from the empirical potential. The relative kinetic energies are as indicated. The cross sections given in parentheses are corrected for the imperfect initial state preparation

j_k^{ϵ}	280 cm ⁻¹		485 cm ⁻¹	
	calc.	exp.	calc.	exp.
2 ₁ ⁻	8.13(7.95)	5.14	5.99(5.85)	5.65
2 ₁ ⁺	4.47(4.65)	6.91	3.16(3.30)	3.86
3 ₁ ⁺	1.69(1.64)	0.97	2.24(2.17)	1.40
3 ₁ ⁻	0.76(0.80)	1.48	0.69(0.77)	1.41
4 ₁ ⁻	0.30(0.29)	–	0.72(0.68)	–
4 ₁ ⁺	0.01(0.03)	–	0.05(0.08)	–
2 ₂ ⁻	0.07(0.71)	1.30	0.03(0.51)	1.54
2 ₂ ⁺	12.88(12.24)	14.13	9.50(9.02)	7.91
3 ₂ ⁺	7.22(6.91)	3.53	5.59(5.36)	4.37
3 ₂ ⁻	1.12(1.43)	2.79	1.10(1.32)	2.01
4 ₂ ⁻	0.78(0.77)	1.06	1.02(1.01)	1.23
4 ₂ ⁺	0.69(0.69)	–	0.84(0.85)	–
5 ₂ ⁺	0.04(0.04)	–	0.09(0.09)	–
5 ₂ ⁻	0.04(0.04)	–	0.14(0.14)	–
4 ₄ ⁻	1.08(1.14)	0.88	1.14(1.21)	1.27
4 ₄ ⁺	2.24(2.18)	2.66	2.39(2.32)	2.16
5 ₄ ⁺	0.96(0.92)	0.49	1.83(1.74)	1.29
5 ₄ ⁻	0.07(0.12)	–	0.20(0.29)	0.77
5 ₅ ⁺	0.08(0.10)	–	0.06(0.10)	–
5 ₅ ⁻	0.56(0.53)	–	0.73(0.70)	–
Q^a	32%		19%	

^a For the cross sections from the scaled ab initio potential [3] these errors are 16% and 36%, respectively.

Ref. [3], are given for comparison. The experimental error in the individual cross sections is estimated to lie between 10% for the larger values and 20% for the smallest ones.

For ortho-NH₃ the cross sections for excitation to the $k=0$ states are predicted better by the empirical potential for both energies; especially the probability of transitions to 2₀⁺, which is overestimated by a factor of two by the ab initio potential, comes out very well. As for transitions to states with $k=3$, the empirical potential overestimates cross sections to states with $\epsilon=-$ and underestimates them to states with $\epsilon=+$. The ab initio potential tends to underestimate all these cross sections, irrespective of the value of ϵ . The overall impression for ortho-NH₃ is therefore that the empirical potential performs better, for both energies. This is reflected in the values of the errors Q .

Whereas for ortho-NH₃ a comparison of the cross sections for the two potentials is hardly affected by the total collision energy, for para-NH₃ it has a large influence. In the lower energy case the scaled ab initio potential is in very good agreement with the experimental data, giving the correct relative magnitude for transitions to the \pm inversion states in all cases. The empirical potential does not predict this relative magnitude correctly for $j_k=2_1$ and 3_1 . Moreover, the transition to 3₂⁺ is too large by a factor of two.

At a relative kinetic energy of 485 cm⁻¹ the situation is almost exactly the opposite: the empirical potential gives the correct relative magnitudes, whereas the ab initio potential predicts them incorrectly to the $j_k=2_1$ states. These observations are supported by the values of Q , which are almost interchanged.

Summarizing, we conclude that the cross sections obtained from the empirical potential are generally in better accordance with experiment than those obtained from the scaled ab initio potential. Moreover the error as defined in Eq. (2), is more constant for the empirical potential, about 26% on average. This seems satisfactory, bearing in mind that the experimental error in the individual cross sections is estimated to be 10% to 20%. Apparently, the detailed description of bound states, as characterized by the vibration-rotation-tunneling spectra, imposes such stringent restrictions on the shape of the empirical potential, that it can adequately reproduce scattering data as well.

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