

He–HF scattering cross sections from an ab initio SAPT potential: confrontation with experiment

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Abstract

Differential and integral cross sections for elastic and rotationally inelastic He–HF scattering are obtained by means of converged close-coupling calculations from an ab initio potential computed by symmetry-adapted perturbation theory (SAPT). These results are compared with total differential cross sections from crossed-beam time-of-flight measurements and with state-to-state integral cross sections for the rotational excitation of HF by collisions with He. It is found that the SAPT potential, which was already shown to be accurate in a comparison with the high-resolution infrared spectrum, yields accurate scattering cross sections as well. A slight scaling in the anisotropy of the potential, which gave better line widths in the spectrum for those levels that undergo rotational predissociation, gives a marginal improvement of the rotationally inelastic cross sections.

1. Introduction

The intermolecular potentials of several atom-molecule dimers: Ar–H₂ [1,2], He–HF [3,4], He–CO [5,6], Ne–CO [7], He–C₂H₂ [8], and Ne–C₂H₂ [9], have recently been calculated ab initio by symmetry-adapted perturbation theory (SAPT), with the inclusion of intramolecular electron correlation. We believe that these potentials are accurate to within 2 to 4% over the full range of distances for which they were given and for all angles. For most of these systems the accuracy of the SAPT potential has already been demonstrated in a computation of the bound states of the dimer and its infrared spectrum, which can be compared with the spectrum measured in a molecular beam [10] or gas cell [11–13] exper-

iment. These bound states and spectra probe mainly the region of the Van der Waals well in the potential surface, which is the most difficult part to compute accurately because the position and depth of this well depend sensitively on the balance between the long-range attractive forces and the mainly repulsive short-range overlap effects. Whether the potential is indeed reliable over a wider range of angles and distances can be checked by comparison with scattering experiments. Computations of the relevant scattering cross sections are then required and, in order to avoid any loss of accuracy in going from the potential to these cross sections, one should use a converged close coupling approach. In the present paper we describe such calculations for He–HF and we confront the results with measured scattering cross sections.

He–HF is the system where the comparison of the infrared spectrum computed from the ab initio SAPT potential with the measured spectrum could be made

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in the greatest detail, because this spectrum was obtained for He–HF and He–DF dimers in a molecular beam in high resolution [10]. It was found [4] that all the transition frequencies from bound state calculations with the SAPT potential [3] agreed to within about 0.1 cm^{-1} with the experimental spectrum. This shows that this potential is indeed very accurate in the region of the well and for all values of the angle (note that the hindered rotations of HF in this dimer extend over the full angular range). Some of the excited levels in the spectrum are quasi-bound, rotationally predissociating states; the lifetimes of these states, i.e., the line widths of the corresponding transitions, were determined [10]. The SAPT potential gave line widths that are systematically too large by about a factor of two. It follows from the Fermi Golden Rule that these line widths are mainly determined by the $P_1(\cos \theta)$ term in the Legendre expansion of the potential, i.e., the first (relatively small) anisotropic term. The reduction of the exponential short-range contribution to the R -dependent coefficient of this term by about 5% yielded line widths that were all within the experimental error bars. This changed the overall potential by about 2% in the well region and 4% in the repulsive region, and did not deteriorate the agreement between the calculated and the measured frequencies. The observed deviations of these frequencies from the values for freely rotating HF (or DF) are mainly determined by the even terms in the Legendre expansion, especially (but not exclusively) the $P_2(\cos \theta)$ term. The spectral line widths did not fully determine the scaling of the $P_1(\cos \theta)$ term, however. The experimental data could be reproduced either by a 5% reduction of the short-range contribution to this term or by a 25% increase of the coefficient $C_{7,\text{disp}}^1$ in the long-range dispersion contribution. One of the goals of the confrontation with scattering experiments is to find out whether this slight scaling makes the ab initio SAPT potential indeed more accurate and whether the scattering cross sections can discriminate between the different ways of scaling the $P_1(\cos \theta)$ term.

Two types of scattering cross sections are available for He–HF, which provide more or less complementary information on the potential surface. Total differential cross sections over a range of scattering angles from 0 to 40 degrees have been determined by Boughton et al. [14] and by Frick et al. [15,16] with crossed beam scattering and time-of-flight measure-

ments for energies of 359, 688, and 709 cm^{-1} . These cross sections show detailed Fraunhofer diffraction oscillations and are sensitive mainly to the isotropic potential [14]. Nesbitt and coworkers [17,18] have recently measured integral cross sections for rotational transitions of HF induced by collisions with He in a crossed jet apparatus with infrared absorption detection. These rotationally inelastic state-to-state cross sections probe in particular the anisotropy of the potential surface in the repulsive region. A number of scattering calculations on He–HF were performed already some time ago [14,19–24], but these calculations used more approximate potential surfaces and, with the exception of Refs. [23,24], also more approximate scattering methods such as the infinite-order sudden or coupled states approximations. The best potential used in these theoretical studies was the HFD (Hartree–Fock plus dispersion) potential of Rodwell et al. [25]. This potential had to be scaled to make the well deeper by about 20% in order to get better agreement with the total differential cross sections [14]. The same potential was used by Lovejoy and Nesbitt in their studies of the infrared spectrum [10]; they had to perform a similar remodeling of the potential to make it significantly more attractive. But, in this case, the scaling of the isotropic long-range coefficients was only about 10%, and the scaling of the corresponding anisotropic coefficients was about 25%. We will now present our close-coupling calculations for He–HF with the ab initio SAPT potential.

2. Close coupling results: comparison with experiment

The potential is described in detail in Ref. [3]. It was obtained by the SAPT method described in Ref. [26], which gives explicitly the individual electrostatic, induction, dispersion, exchange, exchange-induction, and exchange-dispersion contributions to the potential. Each contribution was expanded in a Legendre series

$$V(R, \theta) = \sum_{\lambda=0}^{\lambda_{\max}} v_{\lambda}(R) P_{\lambda}(\cos \theta), \quad (1)$$

with θ being the angle between the HF axis (pointing from F to H) and the vector \mathbf{R} which points from

the HF center of mass to the He nucleus. The coefficients $v_\lambda(R)$ of the exchange and electrostatic charge penetration contributions were analytically fitted by exponential functions of R , those of the long-range induction and dispersion terms by a power series in R^{-n} , with exponential damping functions to account for charge penetration effects. The coefficients $C_{n,\text{ind}}^\lambda$ and $C_{n,\text{disp}}^\lambda$ in the power series were not fitted, but were independently obtained from calculations of the induction and dispersion interactions in the multipole expansion. All parameters in the fit were completely determined by the ab initio calculations, for three different values of the HF bond length r . Here, we use the potential for fixed $r = r_e = 1.7328$ bohr. This potential has a global minimum with $D_e = 39.68$ cm $^{-1}$ for the linear He–HF geometry ($\theta = 0^\circ$) at $R_e = 6.16$ bohr and a secondary minimum with $D_e = 36.13$ cm $^{-1}$ for the linear He–FH geometry ($\theta = 180^\circ$) at $R_e = 5.59$ bohr.

The scattering calculations were performed by the well known close-coupling method with the program HIBRIDON [27]. The reduced scattering mass is 3.3353 amu, the HF rotational constant B equals 20.5597 cm $^{-1}$ [28]. Angular channels were always included up to $j = 9$ inclusive and partial waves up to $J = 200$. For the collision energies of 384, 480, and 576 cm $^{-1}$ which were used for comparison with the experiments of Nesbitt and coworkers [18] (at the energy of 480 cm $^{-1}$ with about 20% spread) the channels with $j \leq 3, 4$, and 4 are open, respectively. For the collision energy of 709 cm $^{-1}$ used in the experiment of Frick et al. [15,16] the channels are open up to and including $j = 5$. Since in the latter experiment not all the HF molecules in the beam were in the ground ($j = 0$) state, we have made calculations with total energies of 708.96, 750.08, and 832.32 cm $^{-1}$, for the initial HF states with $j = 0, 1$ and 2, respectively, and we have averaged the cross sections for scattering from these initial states with the populations 0.347, 0.470, and 0.182 determined experimentally [15,16]. At the lower energies we used the log-derivative propagator in HIBRIDON from $R = 3.5$ to 9.5 bohr with a stepsize of 0.02 bohr and the Airy propagator from 9.5 to 120 bohr, for the higher energies the inner boundary was taken at 2.5 bohr (actually 3.0 bohr would have been sufficient). All these parameters are such that the cross sections from the close-coupling

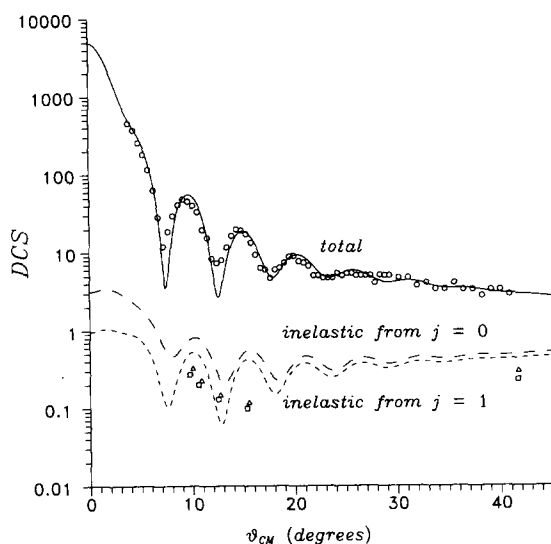


Fig. 1. Total differential cross sections (in Å 2) at collision energy 709 cm $^{-1}$ in the center of mass frame from close-coupling calculations with the ab initio SAPT potential. The circles are experimental data from Refs. [15,16]. The dashed curves are the total inelastic contributions from the initial states with $j = 0$ (long dashes) and $j = 1$ (short dashes), respectively. The squares (for $j = 0$) and triangles (for $j = 1$) are the estimated upper limits for these contributions from Refs. [15,16].

calculations are very well converged. We made some test calculations in which the centrifugal distortion of the HF molecule was included, with the distortion constant $D = 2.1199 \times 10^{-3}$ cm $^{-1}$ [28]. The largest effects of this distortion were found in the inelastic contributions to the differential cross sections at small angles, but even these effects were always smaller than 1%. The effects of the HF distortion on the actually observed quantities were found to be much smaller, so we have neglected these effects.

The results for the total, i.e. elastic plus inelastic, differential cross sections calculated with the ab initio SAPT potential are shown in Fig. 1. We compare these results with the experimental data of Frick et al. [15,16] taken at the same energy of 709 cm $^{-1}$, since these data were given not only in the laboratory frame, but also in the center of mass frame. One observes in Fig. 1 that the agreement between theory and experiment is good indeed; the diffraction oscillations occur at the correct positions and the shoulder at a scattering angle of about 5 degrees which is caused by the rotational rainbow effect is well represented by the cal-

Table 1

State-to-state integral cross sections (in Å²) for He–HF from close-coupling calculations on the ab initio SAPT potential and on the potentials with the $P_1(\cos\theta)$ term scaled either at short range (SR) or at long range (LR). The experimental data and the numbers in parentheses are relative state-to-state integral cross sections

	Ab initio 384 cm ⁻¹	Ab initio 480 cm ⁻¹	Ab initio 576 cm ⁻¹	SR scaled 480 cm ⁻¹	LR scaled 480 cm ⁻¹	Experiment [18] 480 cm ⁻¹ ± 20%
$\sigma_{0 \rightarrow 1}$	4.226 (79.3%)	4.469 (72.7%)	4.552 (67.1%)	3.240 (71.7%)	3.346 (71.0%)	72 ± 7%
$\sigma_{0 \rightarrow 2}$	0.947 (17.8%)	1.413 (23.0%)	1.864 (27.5%)	0.918 (20.3%)	1.032 (21.9%)	21 ± 2%
$\sigma_{0 \rightarrow 3}$	0.159 (3.0%)	0.241 (3.9%)	0.289 (4.3%)	0.335 (7.4%)	0.311 (6.6%)	6.6 ± 0.9%
$\sigma_{0 \rightarrow 4}$	–	0.024 (0.4%)	0.076 (1.1%)	0.022 (0.5%)	0.023 (0.5%)	0.6 ± 0.3%
σ_0^{incl}	5.332	6.147	6.780	4.516	4.712	5.9 ± 0.7

culations. Actually it would have been better for the comparison with the measurements to convert our results to the laboratory frame, but then we would also need to know the details of the apparatus in order to correct the calculated results for the experimental averaging effects. In Ref. [14] it is shown, for example, that as a result of this experimental averaging the dips in the calculated cross sections become shallower and less sharp (see Fig. 4 of this reference). If one takes this effect into account, it seems that the amplitudes of the oscillations in our calculated cross sections are very realistic.

For the case of He–HF the inelastic contributions to the differential cross sections could not be individually derived from the time-of-flight measurements [15,16]. Only upper limits for the total inelastic contributions from the initial states with $j = 0$ and with $j = 1$ could be estimated from these measurements. These contributions are also displayed in Fig. 1, together with the corresponding calculated results. The latter surpass the limits deduced from the experiments for all scattering angles, which would imply that our integral cross sections for these rotationally inelastic processes would be too large as well. In view of the very good agreement of our state-to-state cross sections for rotational transitions with the detailed experimental data of Nesbitt and coworkers, discussed below, we believe that our calculated results are realistic, and that the upper limits given in Refs. [15,16] are probably not very accurate.

We mentioned in the introduction that the SAPT potential could be slightly improved by a 5% reduction of the exponential short-range contribution to the $P_1(\cos\theta)$ term, on the basis of the lifetimes for rotational predissociation. The effect of this scaling on

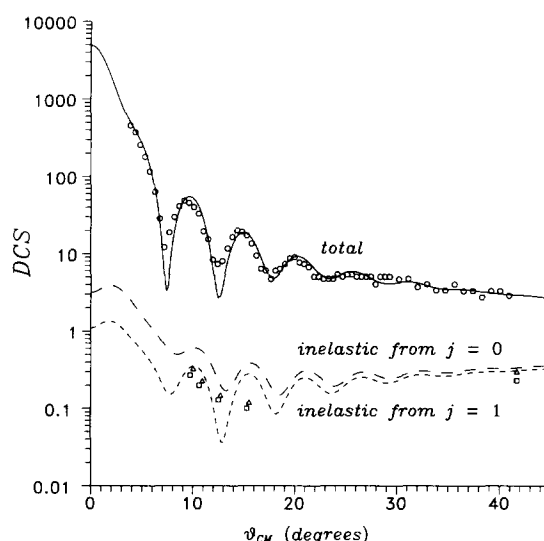


Fig. 2. Total differential cross sections and inelastic contributions calculated with the exponential short-range contribution to the $P_1(\cos\theta)$ term in the potential scaled by a factor of 0.95. For further details, see the caption of Fig. 1.

the total differential cross sections can be observed in Fig. 2. The inelastic contributions are slightly reduced with respect to those in Fig. 1, especially at larger angles, but they are still higher than the upper limits estimated in Refs. [15,16]. The effect on the total cross sections is so minute that it will not be observable. We have also computed the cross sections with a potential that was scaled by a factor of 1.25 in the coefficient $C_{7,\text{disp}}^1$ of the long-range dispersion contribution to the $P_1(\cos\theta)$ term. This scaling has the same effect on the cross sections as the scaling of the short-range contribution to this term; even the inelastic contributions are indistinguishable from those in Fig. 2. Therefore,

its effect on the total cross sections will be negligible as well.

In Table 1 we compare our state-to-state cross sections for rotational excitation of HF by collisions with He with the experiment of Nesbitt and coworkers [18]. The experimental data are the ratios of the inelastic cross sections starting from the ground $j = 0$ state, as well as the total inelastic cross section in Å². The experimental collision energy was 480 cm⁻¹, with a spread of about ±20% due to the angular divergence of the two crossed jets. So we present our cross sections calculated from the ab initio SAPT potential at the energies of 480 cm⁻¹ ± 20%. The values for 480 cm⁻¹ are in good agreement with the experimental data; it seems that the agreement might become even better if one would include some averaging over the energy. The scaling in the $P_1(\cos \theta)$ term of the SAPT potential gives a further improvement of the relative state-to-state cross sections (especially $\sigma_{0 \rightarrow 3}$), but the total inelastic contribution becomes slightly too small.

3. Conclusion

From the results of converged close-coupling calculations for He–HF scattering presented in this Letter it may be concluded that the ab initio SAPT potential [3], of which it was shown already [4] that it describes the bound states and infrared spectrum of He–HF very well, also gives good results for the total differential and the rotationally inelastic state-to-state cross sections. This demonstrates that this potential is not only accurate in the region of the Van der Waals well, but over a wider range of distances including the repulsive region up to several hundreds of wavenumbers. The small 2 to 4% change in this potential which was introduced empirically to make the widths of the rotationally predissociating states agree with the line widths measured in the infrared spectrum, leads to a small change of the inelastic state-to-state integral cross sections and of the inelastic contributions to the differential cross sections, but not to an observable change in the total differential cross sections. The different ways of scaling the $P_1(\cos \theta)$ term of the potential, either at short range or at long range, give only marginal differences in the inelastic cross sections. It will be very useful if, by measurements

of the full Doppler profile, the experiment of Nesbitt and coworkers [17,18] would provide also the state-to-state *differential* cross sections for rotational excitation. Then it might become possible to improve the He–HF potential by varying parameters in the analytic form of the ab initio SAPT potential and fitting these parameters to the experimental data. One should realize, however, that such improvements of the SAPT potential concern only the remaining 2 to 4% inaccuracy.

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