Vibrational and rotational energy transfer in collisions of vibrationally excited HF molecules with Ar atoms

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This work presents converged vibrational close coupling-rotational coupled states calculations of cross sections and rate constants for rotational and vibrational transitions in collisions of vibrationally excited HF molecules with Ar atoms. Reduced channel basis sets assuming both a lower and an upper cutoff in vibrational quantum number are used for calculations at high internal energies of the diatomic molecule. The most recent potential energy surface is employed for the calculations and the correspondence of the results to the previous investigation of rovibrational dynamics in collisions of HF($v=1$) with Ar is examined. It is shown that initial vibrational excitation stimulates vibrationally inelastic transitions to a great extent while the rotational energy transfer is essentially unaffected by initial $v$-number. The cross sections for vibrational relaxation of different vibrational levels of HF are shown to exhibit a strong dependence on initial rotational energy which is, however, of different magnitude for different vibrational states. The dependence of the vibrational relaxation of HF($v=1,3,6$) on the translational energy of the atomic collision partner is different by an energy independent factor for different vibrational levels in the high energy limit and shows minima at low collision energies. © 2001 American Institute of Physics. [DOI: 10.1063/1.1378815]

I. INTRODUCTION

Many experimental studies of Ar+HF inelastic collisions have been performed to provide data for hydrogen fluoride chemical lasers,1–3 investigate mechanisms underlying detailed energy transfer4–6 or test and refine interaction potential energy surfaces.5,6 While the experiments agree well for low rotational and vibrational states of HF, the techniques for measurement of collision cross sections in vibrationally excited HF+Ar meet with certain difficulties leading sometimes to controversial results. For example, Barnes et al.7 have reported that rotational energy transfer in Ar+HF($v=1$) and HF($v=2$) collisions is essentially independent of the initial vibrational state, whereas the results of Copeland et al.,5 who measured rotational relaxation of HF($v=2$) by Ar, have arrived at rates that are only half those obtained by Hinchen and Hobbs8 for the $v=1$ state of HF. At the same time, BelBruno and co-workers10 have inverted the argon-broadened HF infrared linewidths to obtain rate constants for rotational energy transfer in the $v=0,1,2$ states of HF. Their results have shown that rotational transition intensities increase with vibrational excitation. Vibrational relaxation (VR) of vibrationally excited ($v \geq 2$) HF by Ar has not been measured accurately, but the experiments with other collision partners revealed some interesting phenomena such as a rapid increase of VR rates with initial vibrational excitation and a significant variation of this dependence with nature of the collision partner. Smith and Wrigley2 measured upper bounds of the rate constants for VR of HF($v=3,4,6$) in collisions with Ar which are also increasing with initial $v$ number.

Several experimental studies of rotationally inelastic Ar+HF scattering have been accompanied by rigorous close coupling and coupled states calculations on various potential energy surfaces (PES).4,6,13,14 These calculations, showing an impressive agreement with experimental data, provided a detailed understanding of Ar+HF interaction and assisted interpretation of many interesting observations like the velocity structure in the collisionally excited Doppler profiles9 or the shoulder behavior of inelastic differential cross sections.13 Most theoretical studies of rotational transitions in Ar+HF collisions have, however, been limited to the ground and first excited vibrational states of HF and no systematic investigation of rotational energy transfer in vibrationally excited HF+Ar has been performed to our knowledge. Theoretical studies of vibrationally inelastic Ar+HF collisions have been hampered by the lack of a reliable three dimensional PES and most of the works are of model character.15,16 Thompson17 has performed quasiclassical trajectory calculations of vibrational and rotational relaxation of HF at three vibrational and several rotational states on a highly approximative model potential. His results indicated that rotational energy transfer is not affected by initial vibrational excitation and the dominant energy transfer pathways are R−T and V−T at considered collision energies. In the preceding work,18,19 denoted hereafter as Paper I, we have performed vibrational close coupling-coupled states (VCC-CS) calculations of experimentally observable rate coefficients for rotational and vibrational energy transfer in Ar+HF collisions on a newly developed three-dimensional PES.20 The results of Paper I have illustrated that (1) VR of HF($v=1,j$) has a quasiresonant character leading to a predominant population of the two energetically nearest rotational levels of
\(v = 0\) after collision; (2) vibrationally inelastic transitions in the \(\text{Ar} + \text{HF}(v = 1)\) collisions are 5–6 orders of magnitude less probable than rotationally inelastic ones; (3) vibrational excitation of HF up to the level \(v = 4\) as well as rotational excitation of \(\text{HF}(v = 1)\) increase VR rates to a great extent.

The main goal of the present work is to extend the calculations of Paper I to even higher vibrational energies of HF and observe the correspondence of the dynamics of rovibrational energy transfer in highly excited diatomic molecule to that of HF in its low vibrational states. For this purpose we perform the VCC-CS calculations with a reduced number of open channels implying an expansion of partial wave functions in an energetically local basis set. This allows efficient calculations of converged cross sections for rovibrational transitions in HF excited up to \(v = 12\). At various levels of vibrational excitation of HF we investigate the competition of vibrational and rotational energy transfer and the role of vibrational, rotational and translational energy for VR in \(\text{Ar} + \text{HF}\) collisions. The rate constants for one quantum rotational relaxation of several rotational levels of HF in three vibrational states are also computed using the rigorous close coupling and coupled states formalisms and compared with the previously available data by BelBruno and co-workers\(^{10}\) obtained by inversion of the argon broadened HF spectral widths.

The dynamical calculations of the present work are briefly reviewed in Sec. II and the results are presented in Sec. III. Section IV summarizes the conclusions. A discussion of convergence of the reduced channel calculations at high internal energies of the diatomic molecule is given in the Appendix.

**II. DYNAMICAL CALCULATIONS**

For dynamical calculations of the present work we use the \(J\)-labeled variant of the vibrational close coupling-coupled states approach as developed and described by Pack.\(^{24}\) The details of the calculations for the present \(\text{Ar} + \text{HF}\) system are given in Paper I. Very briefly, the coupled states approximation (CSA) (Ref. 24) is applied to the centrifugal term in the total Hamiltonian and the partial wave functions (\(\Psi^{J\Omega}\)) are expanded in terms of products of translational (\(F_{vj'}^{(\Omega)}\)), vibrational (\(\chi_v^j\)) and rotational (\(Y_{J\Omega}\)) functions as follows:

\[
\Psi^{J\Omega} = \frac{1}{R} \sum_{v = 0}^{\nu + n} \sum_{j} F_{vj'}^{(\Omega)}(R) \chi_v^j(r) Y_{J\Omega}(\Theta, 0),
\]

where \(v\) denotes the initial vibrational level, \(n\) is a positive integer, and the second summation is performed over all rotational states \(j\) of the given vibrational level up to a specified energy limit. The number of vibrational states in the basis set is thus normally equal to \(2n + 1\), \(n\) being determined by both the collision system and the internal energy of the diatomic molecule (see Appendix). \(R, r,\) and \(\Theta\) in the above equation denote the conventional Jacobi coordinates representing the \(\text{Ar}–\text{HF}\) center of mass separation, HF bond length, and the angle between the vectors corresponding to \(r\) and \(R\) as shown, e.g., in Fig. 1 of Paper I. Substitution of expansion (1) into the stationary Schrödinger equation leads to a system of CC–CS equations to be solved for fixed values of the total angular momentum for the collision \((J)\) and its projection onto the body fixed quantization axis \((\Omega)\),

\[
\frac{d^2}{dR^2} + k_v^2 - J(J + 1) - j(j + 1) - 2\Omega^2 \frac{L}{R^2} F_{vj'}^{(\Omega)}(R) = 2\mu \sum_{v', J'} \langle v J | V(r, R, \Theta) | v' J' \rangle F_{v' j'}^{(\Omega)}(R).
\]

The 3D PES \(V(r, R, \Theta)\) entering the matrix elements in Eq. (2) is expanded in a Legendre series that allows us to evaluate the integrals over rotational wave functions analytically.\(^{25}\) The integrals over the vibrational wave functions are evaluated numerically using a 50 point Gauss–Hermite quadrature scheme. The asymptotic solution of Eq. (2) yields a scattering \(S\)-matrix from which the total cross sections for rovibrational transitions are derived. To compute the \(S\)-matrix elements describing the probability for the \(j \rightarrow j'\) transitions at a given value of \(J\) the calculations are performed at \(m + 1\) values of \(\Omega\) \((\Omega = 0, \ldots, m)\), \(m\) being equal to \(\text{min}(J, j, j')\). No distinction between different parities is made within the CS approximation and all \(S\)-matrix elements for \(\Omega \neq 0\) are multiplied by 2.

The \(J\)-labeled CS approach\(^{24}\) has been chosen for the present work due to its simplicity and relatively low compu-
tional costs. An alternative $l$-labeled formulation of the CS approximation originally developed by McGuire and Kouri\textsuperscript{26} and investigated and used by many researchers\textsuperscript{27,28} is known to give better results for orientation dependent quantities.\textsuperscript{28} Being interested in the averaged quantities and mostly qualitative analysis in this paper, we believe that the $J$-labeled approach is acceptable for the present purposes. As has been pointed out by the referee of the present manuscript, the CS approximation is based on derivations using an incorrect kinematic law.\textsuperscript{29} Thus, it is not possible to reliably assess the accuracy of the CS approximation. Notwithstanding this difficulty, Refs. 24, 27, 28, as well as many other works show that the CS approach can be used as a computational method providing the results are tested by comparison with more rigorous calculations in every particular case.

The rovibrational energy levels of HF as well as the vibrational wave functions depending on rotational quantum numbers are obtained by numerical solution of the Schrödinger equation for the diatomic molecule. The HF interaction potential, taken from the work of Stark and Werner,\textsuperscript{30} is in the form of an extended Rydberg function that provides energy levels close to the experimentally determined values.\textsuperscript{20} The potential used in the current study is based on a correct potential available experimental rate constants for rotational and vibrational relaxation of HF in collisions with Ar has been demonstrated in Paper I where we also discuss the accuracy of the coupled states approximation with reference to the data available in the literature. In addition, we compare in Table I the rate constants for one quantum rotational relaxation ($j\rightarrow j-1$) of HF in several vibrational and rotational states calculated with the coupled states method and the rigorous close coupling approach treating the projection of the angular momentum ($\Omega$) accurately. Only one vibrational state is considered in the basis set for these calculations that give, in accord with the results presented in the Appendix, the fully converged cross sections. The coupled states results deviate from the corresponding close coupling values by not more than 30% in the worst case and the accuracy of the coupled states approximation improves with initial $j$-number.

The accuracy of the coupled states approximation is the same for all three vibrational levels considered. The data of BelBruno and co-workers,\textsuperscript{10} obtained by inversion of the argon-broadened HF infrared linewidths, are also shown in Table I. Our close coupling results differ from the values by BelBruno and co-workers by a factor of 2.5 at low initial $j$-values and approach the inverted rate constants at higher rotational states where the agreement is to within a few percent. We find the overall agreement good since similar calculations of rotational relaxation rates in pure HF in the earlier work of BelBruno et al.\textsuperscript{10} differ from the available classical trajectory data by two orders of magnitude and in the case of Ar+HF collisions the authors\textsuperscript{10} used somewhat noisy data for the linewidths.

### III. RESULTS

In order to perform the close coupling-coupled states calculations of cross sections for rotational and vibrational energy transfer in vibrationally excited HF+Ar we expand the total wave function in Eq. (1) in terms of energetically local basis states that lead us to ignore low energy vibrational states making an apparently small contribution to the dynamics of the given vibrational level of HF. The convergence of such reduced channel coupled states calculations is discussed in the Appendix. All calculations of the present section, except when HF is initially in the vibrational states $\nu=11$ and $\nu=12$, are converged to within 1% with respect to the number of vibrational basis states, the parameters of the integration of the coupled equations and the number of partial waves. For the dynamics of HF($\nu=11$) and HF($\nu=12$) the calculations are converged to within 10%.

#### Table I. Room temperature ($T=300$ K) rate constants in units of cm$^3$ s$^{-1}$ molecule$^{-1}$ for one quantum rotational relaxation in HF($\nu$) + Ar, $k_{j\rightarrow j-1}$.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>CC–CS method</th>
<th>CC method</th>
<th>Ref. 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$0.279\times10^{-10}$</td>
<td>$0.392\times10^{-10}$</td>
<td>$1.148\times10^{-10}$</td>
</tr>
<tr>
<td>1</td>
<td>$0.366\times10^{-10}$</td>
<td>$0.493\times10^{-10}$</td>
<td>$1.156\times10^{-10}$</td>
</tr>
<tr>
<td>2</td>
<td>$0.413\times10^{-10}$</td>
<td>$0.557\times10^{-10}$</td>
<td>$1.193\times10^{-10}$</td>
</tr>
<tr>
<td>$v=1$</td>
<td>$0.381\times10^{-10}$</td>
<td>$0.424\times10^{-10}$</td>
<td>$1.003\times10^{-10}$</td>
</tr>
<tr>
<td>3</td>
<td>$0.554\times10^{-10}$</td>
<td>$0.562\times10^{-10}$</td>
<td>$0.693\times10^{-10}$</td>
</tr>
<tr>
<td>4</td>
<td>$0.439\times10^{-10}$</td>
<td>$0.430\times10^{-10}$</td>
<td>$0.440\times10^{-10}$</td>
</tr>
<tr>
<td>5</td>
<td>$0.327\times10^{-10}$</td>
<td>$0.392\times10^{-10}$</td>
<td>$0.285\times10^{-10}$</td>
</tr>
<tr>
<td>$v=2$</td>
<td>$0.345\times10^{-10}$</td>
<td>$0.404\times10^{-10}$</td>
<td>$1.053\times10^{-10}$</td>
</tr>
<tr>
<td>3</td>
<td>$0.566\times10^{-10}$</td>
<td>$0.574\times10^{-10}$</td>
<td>$0.773\times10^{-10}$</td>
</tr>
<tr>
<td>4</td>
<td>$0.467\times10^{-10}$</td>
<td>$0.484\times10^{-10}$</td>
<td>$0.528\times10^{-10}$</td>
</tr>
<tr>
<td>5</td>
<td>$0.360\times10^{-10}$</td>
<td>$0.382\times10^{-10}$</td>
<td>$0.388\times10^{-10}$</td>
</tr>
</tbody>
</table>

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It has been shown in Paper I that the vibrational relaxation of HF\((v, j = 0)\) by Ar has a quasiresonant character leading to a predominant population of the energetically nearest levels of the ground vibrational state. Figure 1 shows the final rotational distributions of HF after one quantum vibrational relaxation of various \(|v, j = 0\rangle\) states in collisions with Ar. The quasiresonant character of vibrational relaxations persists when the diatomic molecule is vibrationally excited to as high a level as \(v = 12\). Although the relative populations of different \(j\)-levels after VR of the \(|v, j = 0\rangle\) states depend on the interaction anisotropy and relative spacing of the rotational levels, which both change with the \(v\)-number, the general shape and relative magnitude of the peaks in the final rotational distribution after VR of different vibrational states remain similar.

It may also be seen from Fig. 1 that the absolute values of cross sections for vibrationally inelastic transitions increase by several orders of magnitude with an increase of the initial excitation of the HF molecule to high vibrational states. Figure 2 shows the dependence of cross sections for one quantum rotational transitions, multiple quantum rotational transitions and one quantum vibrational relaxation upon the initial vibrational quantum number calculated at collision kinetic energy 1300 cm\(^{-1}\). The one and two quantum rotational transitions are almost independent of the vibrational energy whereas the cross sections for one quantum vibrational relaxation increase by almost 5 orders of magnitude as the initial vibrational quantum number changes from 1 to 10. The cross sections for many quantum rotational transitions behave similarly to vibrationally inelastic cross sections but show a slower increase with initial vibrational energy. The quantitative information on the dependence of the rotational and vibrational energy transfer on the vibrational quantum number can be obtained from Table II, where we also include the data for initial vibrational states with \(v = 11\) and \(v = 12\). It may be seen that at low levels of vibrational excitation the rotational energy transfer is several orders of magnitude faster than the vibrational energy transfer.

As the initial vibrational energy increases, the vibrational relaxation of the \(|v, j = 0\rangle\) levels starts to compete with rotationally inelastic transitions and even exceeds the multiple quantum rotational transitions at very high levels of vibrational excitation.

We have noted in Paper I that the vibrational relaxation rates in the Ar+HF collisions show a very strong dependence on the initial rotational energy of HF and depend only weakly on the initial kinetic energy of the colliding particles. This supports the idea of Nikitin who suggested that the vibrational energy redistribution in HF+Ar encounters is induced by rotational collisions of the diatomic molecule with the incoming atom. The vibrational relaxation of HF should, therefore, be more determined by the amount of initial rotational rather than by the translational energy. In Fig. 3 we show the cross sections for the \(|v, j\rangle\rightarrow|v-1, \Sigma j'\rangle\) transitions at collision energy 2000 cm\(^{-1}\) for \(v = 1\), \(v = 3\), and \(v = 6\). For comparison purposes all cross sections are divided by the one corresponding to the relaxation of the \(|v, j = 0\rangle\) state: 1.40\(\times\)10\(^{-7}\) \(\AA^2\) \((v = 1)\), 2.81\(\times\)10\(^{-5}\) \(\AA^2\) \((v = 3)\), 8.51\(\times\)10\(^{-2}\) \(\AA^2\) \((v = 6)\).

The collision energy is 2000 cm\(^{-1}\).
by the one corresponding to the relaxation of the \(|v,j=0\rangle\) state. The vibrational relaxation is stimulated by the initial rotational energy for all initial vibrational levels but the dependence on the rotational energy is drastically different, being almost an order of magnitude stronger when the molecule is in the \(v=1\) state than when it is in the \(v=6\) state. The dependence of the vibrational relaxation cross sections on the translational energy of the collision partners (Fig. 4) is similar for HF in the \(v=1, v=3,\) and \(v=6\) states and shows some structure at low collision energies.

The results presented in Figs. 2 and 3 indicate that the mechanism of vibrational energy transfer in Ar+HF collisions apparently changes with increasing initial vibrational energy of the diatomic molecule. When HF is at low vibrational states, its vibration is very stiff and the vibrational transitions are predominantly induced by rotational collisions,\(^{16}\) hence the strong dependence of vibrational relaxation of \(v=1\) on the initial rotational energy (Fig. 3). When the HF molecule is vibrationally excited, however, the absolute magnitude of the direct \(V\rightarrow T\) energy transfer is significantly enhanced and the rotational motion of the diatomic molecule is less important for the vibrationally inelastic transitions. As a result the dependence of vibrational relaxation on the rotational energy of the diatomic molecule is much weaker when HF is initially excited to \(v=6\). A significant increase of vibrational energy transfer with initial vibrational excitation has been also observed by Balakrishnan and co-workers in their quantum mechanical calculations of H+H\(_2\) collisions.\(^{32}\) These authors have analyzed the coupling matrix elements responsible for vibrationally inelastic transitions and illustrated that the matrix elements coupling adjacent vibrational levels are significant over a wider range of \(R\)-distance due to a greater stretching of the diatomic molecule, when H\(_2\) is vibrationally excited. This does not explain, however, why the purely rotational energy transfer is almost not affected by initial vibrational excitation. It might be that the vibrationally elastic rotational transitions in Ar+HF collisions are fully determined by the anisotropy of interaction of Ar with HF which is very large already when HF is at \(v=0\) and increases insignificantly with vibrational excitation of HF. The vibrational motion of the diatomic molecule would then play no role for purely rotational transitions, which is in accord with the results presented in Table III of the Appendix leading to the conclusion that the rovibrational coupling is not important for rotationally inelastic Ar+HF transitions.

**IV. SUMMARY**

In this work we use the vibrational close coupling-coupled states approach to investigate the rotational and vibrational energy transfer in collisions of vibrationally excited HF molecules with Ar atoms. The calculations performed on the most recent PES give results that can be summarized as follows:

1. The vibrational energy transfer from vibrationally excited HF molecules shows a qualitatively similar trend to that from HF at low vibrational levels despite a very large change in cross section. Thus, the quasi-resonant character of vibrational relaxation of HF\((v)\) resulting in an inverse rotational population of HF\((v-1)\) persists to as high a rotational level as \(v=12\) showing similar patterns in the final rotational distribution.

2. The one and few quantum rotational energy transfer is essentially unaffected by the initial vibrational energy, whereas the cross sections for vibrationally inelastic transitions in Ar+HF\((v)\) collisions increase dramatically with the \(v\)-number. As a result, the vibrational relaxation of HF, being 5–6 orders of magnitude slower than rotational energy transfer at low vibrational levels of the diatomic molecule, becomes comparable in magnitude to one and two quantum rotational transitions and faster than the multiple quantum rotational transitions at high vibrational levels.

3. The cross section for vibrational relaxation of HF\((v=1,3,6)\) is shown to increase significantly with initial rota-
tional energy of the diatomic molecule but the dependence is different for different $v$-levels being much stronger in the $v=1$ case.

4. The dependence of cross sections for vibrational relaxation of different $v$-levels of HF on the translational energy of the colliding particles is similar and shows some structure at low translational energies.

ACKNOWLEDGMENTS

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APPENDIX: CONVERGENCE OF REDUCED CHANNEL COUPLED STATES CALCULATIONS

The HF molecule has a very large vibrational frequency and a small moment of inertia. As a result, the rovibrational energy spectrum of HF is very sparse and the vibrationally elastic rotational transitions in Ar+HF collisions have a significantly different nature from the one quantum vibrational transitions, while the one quantum vibrational transitions are several orders of magnitude faster than multiple quantum vibrational transitions. This suggests that if we are interested in the dynamics (rovibrationally or rotationally inelastic) of some high energy $v$ level it may be possible to neglect all vibrational states below $v-n$ and above $v+n$ that correspond to the partial wave expansion Eq. (1). The convergence of the results can then be sought by gradually increasing $n$. It should be noted that all rotational states up to a certain energy limit for each vibrational level must be included in the basis set and the convergence with respect to the number of rotational states should be checked as usual. Below we will focus on the dependence of the results upon the number of vibrational states in the basis implying that the calculations are fully converged with respect to the number of $j$-states.

Table III shows cross sections for vibrationally elastic rotational transitions in the Ar+HF($v,j=0$) collisions at the collision energy 1300 cm$^{-1}$ obtained with different number of vibrational basis states. For all vibrational states considered, the results are almost unaffected by the number of vibrational basis states and the values calculated with only one vibrational state in the basis agree very well with the full CS calculations, in the cases when $v=2$ and $v=4$, and with the larger calculations in the $v=7$ case.

Cross sections for vibrational relaxation (VR) of two vibrational levels of HF obtained with different number of vibrational basis states are collected in Table IV. When the internal energy of HF is rather low ($v=4$) the difference between vibrational levels is very big and the basis of five vibrational states ($v-2,v-1,...,v+2$), that will be denoted hereafter as a $5v$ basis, ensures converged results for one quantum and total VR cross sections. At a higher internal energy of the diatomic molecule ($v=10$) the multiple quantum transitions play a greater role which is due to shrinking of the energy gap between vibrational states with increase of energy. The convergence range with respect to the number of $v$ states is, therefore, larger at high internal energies of HF and it may be seen that a 7$v$ basis ($v-3,v-2,...,v+3$) is necessary to have the cross sections for VR of HF($v=10$) converged to within 1%. We have also performed the convergence tests at higher collision energies and found that the number of vibrational basis states required for converged calculations of VR cross sections in Ar+HF collisions is essentially independent of the collision energy which is again attributed to the large vibrational frequency of HF.

Table III and IV also show the number of vibrational basis states ($N$) that are included in the calculations. The computational effort in solving Eqs. (2) grows with the number of basis states typically as $N^3$. The data of Tables III and IV, therefore, illustrate two important points: (1) a great reduction of the computational costs may be achieved by using the vibrationally reduced channel basis set for calculations of atom–diatom scattering when the diatomic molecule is in high excitation; (2) the dimension of the reduced channel basis set ($N$) is independent of or increases very slowly with the internal energy of the diatomic molecule.

To summarize, the results of the present Appendix are the following: (1) Rovibrational coupling is not important for vibrationally elastic rotational transitions in the Ar+HF collisions and only one vibrational state is needed in the basis set to obtain converged (to within 1% for low vibrational states and 2% for high vibrational states) cross sections for rotational relaxation; (2) Five vibrational states ($v-2,v-1,...,v+2$) in the basis set should be enough for calculation of cross sections for one quantum and total vibrational relaxation of low vibrational states, whereas (3) the number of required vibrational basis states increases with internal energy of HF and the $7v$—or an even larger—basis set should be used for accurate calculations of vibrational relaxation of high vibrational levels.

TABLE IV. Cross sections ($\text{Å}^2$) for vibrational relaxation of HF($v,j=0$) by Ar. The numbers in parentheses denote the vibrational states in the basis and $N$ is the total number of rovibrational basis states. Collision energy is 1300 cm$^{-1}$. The summation convention $\sum j'$ is used for the total $j$-summed cross sections.

<table>
<thead>
<tr>
<th>Basis</th>
<th>$N$</th>
<th>$v,j=0 \rightarrow v,j=0$</th>
<th>$v,j=0 \rightarrow v,j'=1$</th>
<th>$v,j=0 \rightarrow v,j'=2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3,4,5)</td>
<td>72</td>
<td>0.3785 $\times 10^{-3}$</td>
<td>0.1918 $\times 10^{-2}$</td>
<td>0.1918 $\times 10^{-2}$</td>
</tr>
<tr>
<td>(2,3,4,5,6)</td>
<td>118</td>
<td>0.4410 $\times 10^{-3}$</td>
<td>0.4731 $\times 10^{-2}$</td>
<td>0.4784 $\times 10^{-2}$</td>
</tr>
<tr>
<td>(1,2,3,4,5,6,7)</td>
<td>156</td>
<td>0.4378 $\times 10^{-3}$</td>
<td>0.4736 $\times 10^{-2}$</td>
<td>0.4799 $\times 10^{-2}$</td>
</tr>
<tr>
<td>Full CS, ($0,1,...,7$)</td>
<td>193</td>
<td>0.4377 $\times 10^{-3}$</td>
<td>0.4736 $\times 10^{-2}$</td>
<td>0.4799 $\times 10^{-2}$</td>
</tr>
</tbody>
</table>

There is a factor of $(2j+1)^{-1}$ missing in the right-hand side of Eq. (5) in Ref. 18.


R. M. Shroll and J. R. Barker (private communication).

A. A. Buchachenko (private communication).


R. N. Zare, Angular Momentum (Wiley, New York, 1988).


