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Franck–Condon distributions in the Penning ionization of HCl by metastable helium^{a)}

Mattanah S. de Vries, George W. Tyndall, and Richard M. Martin
Department of Chemistry, University of California, Santa Barbara, California 93106

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The nature of reactive collision complexes has been a topic of great interest since the beginning of modern theoretical chemical kinetics. However it has generally not been possible to study these complexes experimentally, because of their transient nature and very low concentrations. In recent years there has been interest in the possibility of using laser spectroscopy to study reaction complexes, but so far the results from this approach have been limited and inconclusive.

The process of Penning ionization offers a unique class of reactions for which experimental data on the reaction complex are readily available. This is because an electron is emitted from the collision complex on a time scale which is fast compared to the motion of the nuclei. Therefore Penning ionization electron spectroscopy (PIES) reveals the state distribution in which the molecular ions are formed in the collision complex. When the molecular ion is formed in a fluorescent excited state, the rovibronic state distribution can also be studied by Penning ionization optical spectroscopy (PIOS). Since fluorescence lifetimes are much longer than collision complex lifetimes, PIOS probes the ions after the dissociation of the complex. Therefore, the rovibronic distributions of the ions determined from PIES and PIOS studies may be different, if the initial distribution is perturbed by the "half-collision" which occurs following ionization in the collision complex. A prominent example is the reaction $\text{He}(2^3S) + \text{HCl} \rightarrow \text{He} + \text{HCl}^+(A^2\Sigma^+) + e^-$. PIES measurements show that $\text{HCl}^+(A)$ is formed with a vibrational population which is close to that expected from Franck–Condon (FC) factors for the $\text{HCl}(X) \rightarrow \text{HCl}^+(A)$ transition.^{1–3} On the other hand, PIOS data, obtained in flowing afterglow experiments by Richardson and Setser,⁴ show a population in which $v' = 0$ is strongly enhanced with respect to the FC distribution. These results have been confirmed in more recent flowing afterglow experiments by Yench.⁵ Several possibilities have been discussed to explain the difference between the PIES and PIOS results.^{1,4} (a) When the He and $\text{HCl}^+(A)$ separate after formation they carry out a half-collision in which vibrational to translational energy transfer may take place. (b) $\text{HCl}^+(A)$ could be formed via an autoionizing state, followed by an optical cascade. (c) The lifetime of $\text{HCl}^+(A)$ is of the order of $2\mu\text{s}$. Therefore, at the pressures of 1 Torr or more employed in flowing afterglow experiments, there might be quenching processes that preferentially depopulate the higher v' levels, or secondary reactions which preferentially produce $v' = 0$.⁶ Explanation (b) is unlikely, since it would yield low energy Penning electrons that were not observed in any of the PIES studies.^{1–3} In order to investigate explanation (a) vs (c) we have conducted crossed molecular beam PIOS experiments in which the product emission spectrum is obtained under single collision conditions.

A modified version was used of an apparatus that has previously been described.⁷ He metastables were formed in a Penning ionization discharge downstream from a supersonic beam source. This method has been found to give $\geq 90\%$ $\text{He}(2^1S)$ metastables.⁸ Light from the $\text{He}^* + \text{HCl}$ interaction region was collected with a quartz lens and focused onto the entrance slit of a monochromator.

Figure 1 shows a portion of the $\text{HCl}^+(A)$ emission spectrum, taken at an average collision energy of 40 meV. Since the vibrational bands are partially overlapped, data analysis was performed by computer simulation of the spectrum, varying the vibrational and rotational population distributions to fit the experimental results. Molecular constants were used as given by Huber and Herzberg⁹ and references therein, with FC factors as calculated by Coxon¹⁰ and upper state lifetimes from Mohlman *et al.*¹ The best fit was obtained with a relative vibrational population v' of 0/1/2/3 = 87/100/78/69 and with rotational temperatures which varied from 600 K for $v' = 0$ to 300 K for $v' = 3$. Emission from $v' > 3$ was also observed, but the signal/noise ratio of these peaks was insufficient to assign reliable populations.

Our $\text{HCl}^+(A)$ vibrational branching ratios are very different from those obtained from flowing afterglow PIOS experiments (100/53/48/41),⁴ and are close to those found in

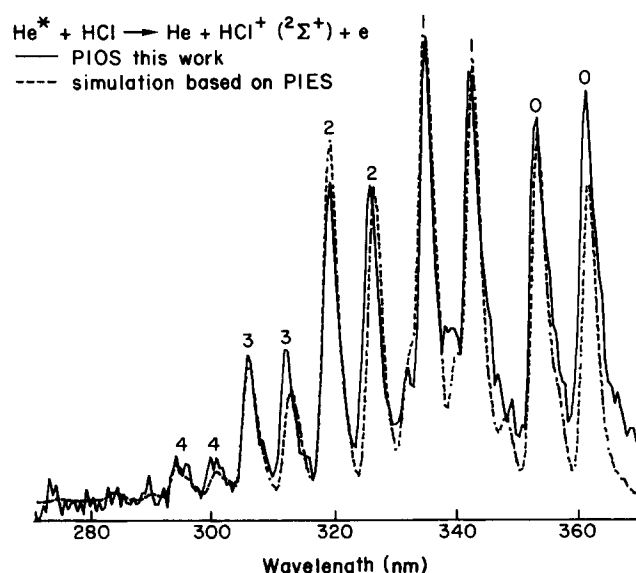


FIG. 1. Emission spectrum obtained in Penning ionization of HCl by He^* . The vibrational levels of the emitting $\text{HCl}^+(A)$ state are indicated for the main peaks. The broken line is a computer simulation of the spectrum based on the product vibrational population found in PIES.

molecular beam PIES (79/100/84/57).¹⁻³ The agreement of our PIOS results and the PIES results is also illustrated by a computer simulation of the spectrum that would result from the population distribution found in PIES, shown in Fig. 1 as a dashed line. This agreement shows that the half-collision from the reaction complex to separated products does not significantly change the $\text{HCl}^+(A)$ vibrational distribution, and indicates that the different distribution found in the flowing afterglow experiments is due to quenching processes or secondary reactions, explanations (c).

The cross sections for ionization of HCl by $\text{He}(2^1S)$ and $\text{He}(2^3S)$ are 145 and 62 \AA^2 at 300 K,¹² corresponding approximately to our collision energy of 40 meV. These large cross sections suggest ionization via a long range electron transfer process. We also measured the $\text{He}(2^1S) + \text{HCl}$ PIOS spectrum at 140 meV collision energy, where the total ionization cross section is about 70 \AA^2 ,^{12,13} and obtained the same result as at 40 meV. This indicates that the HCl potentials are not strongly perturbed in Penning ionization by $\text{He}(2^1S)$ over this collision energy range, which is consistent with the large cross sections (corresponding to a long range process) and with the nearly FC vibrational distribution.

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Symmetry-dependent broadening parameters for methane^{a)}

Kenneth Fox^{b)}

Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200 and Infrared and Radio Astronomy Branch, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771

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Pressure-broadened widths of lines in the infrared spectra of methane are of importance in a variety of contexts.¹ Recently, linewidths for vibrational-rotational $v_3 = 0 \rightarrow 3$ and $J \rightarrow J + 1$ transitions in both $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ were measured at very high resolution.^{2,3} The broadening gases were N_2 , H_2 , and He . Systematic variations as a function of tetrahedral (T_d) symmetry⁴ were found in all cases. These experimental results follow a pattern predicted in earlier calculations of scattering of argon from methane.⁵

There have been a number of computations of pressure-broadened linewidths γ for methane in which the Anderson-Tsao-Curnutte theory was utilized.⁶⁻⁹ One of these works⁸ resulted in significant variations of γ with T_d symmetry. In the particular case of interest here, theoretical values are shown in Table I. These are compared with the present experimental data. It is clear that, for the most part, the latter are substantially larger than the former. More significantly, for purposes of this work, in the theoretical results $\gamma_A < \gamma_E \leq \gamma_F$ for a given J multiplet; while in the experimental, $\gamma_E < \gamma_A \lesssim \gamma_F$.

The experimental results shown here were obtained using the Kitt Peak¹⁰ solar Fourier transform spectrometer, at spectral resolving power on the order of 10^6 , together with a multitraversal absorption cell of 6 m base length.^{2,3} Pressures were determined to an accuracy of ± 0.2 Torr by

means of a Baratron capacitance manometer. The cell temperature, monitored during the experiments, was measured to a few tenths of a K. In separate runs, $^{12}\text{CH}_4$ was broadened by N_2 , H_2 , He , and a mixture of equal parts of H_2 and He ; $^{13}\text{CH}_4$ was broadened by H_2 . The purity of both isotopic methanes was at least 98.8%. Between runs, the absorption cell was flushed with N_2 or H_2 and then evacuated.

The spectroscopic data were analyzed using the AT-MOS computing facility at the Jet Propulsion Laboratory.¹¹ These techniques involved a nonlinear least squares procedure iterating between observed spectra and synthetic spectra calculated under appropriate instrument and gas sample conditions. The spectral line shapes were taken to be Voigt profiles.¹² For each J multiplet, all tetrahedral components were considered simultaneously. In such complex spectra,² we proceeded to use the computer program interactively, allowing changes in the fitted parameters between iterations.

Table II summarizes the measurements for combinations of gases involved in this study. These results are numerical averages of all linewidths corresponding to a given T_d symmetry for $J = 0$ through 6. The data were organized in this manner out of pure serendipity, and the observed systematics were completely unexpected. What emerges is the pattern $\gamma_E < \gamma_A \lesssim \gamma_F$ for all cases studied: γ_E is substantially smaller than γ_A , while γ_A is near to, but significantly