Broadening and shifting of HF absorption lines perturbed by argon: stringent test of classical impact theory

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Two variants [1,2] of the up-to-date classical theory of impact broadening and shifting of isolated spectral lines are applied in widths and shifts calculations of HF vibration-rotational absorption lines perturbed by Ar. The first theory [1] treats HF molecule as a rigid rotor during the collision, so its rotational and vibrational motions are completely decoupled. Although this "rigid" method allows including the vibrational dephasing by means of the difference of HF–Ar interaction potential in different low-lying HF vibrational states, it does not supply all the information which would follow from fully self-consistent "non-rigid" approach. For example, it is known that for highly excited vibrational states, the V-R-T coupling during the collision results in interesting and unusual physics (see, e.g. [3] for H_2–He). The second theory [2] represents the fully self-consistent "non-rigid" method. The primordial Gordon's theory [4] was extended in [2] to the case of non-rigid vibrating rotors to make possible the study of line broadening and shifting in highly excited diatomic molecules. All physical effects influencing collision-induced width and shift of vibration-rotational lines were included into consideration via non-perturbative and self-consistent way. They are: rotational and vibrational dephasing, reorientation of angular momentum, inelastic transitions (R-T, V-R-T, etc.), vibration-rotational coupling. In the present study an exact Hamilton equations of V-R-T motions are employed in trajectory calculations. Very accurate *ab initio* potential energy surfaces (PES) for HF–Ar interactions are used: vibrationally averaged two-dimensional H6(4,3,2) PES of Hutson [5] for "rigid" method and full three-dimensional V_{05} PES of Jankowski [6] for "non-rigid" one. Line widths and shifts are calculated at temperatures 296, 398 and 423 K for 0-0, 0-1 and 0-2 vibrational bands of HF for rotational quantum number J ranging from 0 to 9. Comparison is made with benchmark results of quantum close-coupling calculations of Green and Hutson [7] obtained employing the same PES [5] as well as with experimental data [8]. The comparison demonstrates good accuracy for both "rigid" and "non-rigid" variants of classical theory for all J values except for $J=0$. Our main interest in this study was to test the validity of recently developed self-consistent "non-rigid" classical theory [2] to allow its further confident application to highly excited vibrational states of various diatomic molecules.

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