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COMMENTS

HI Photofragmentation Revisited. Comment on “Probing Excited Electronic States Using Vibrationally Mediated Photolysis: Application to Hydrogen Iodide”

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In our recent studies,[1,2] we have performed a comprehensive theoretical analysis of hydrogen iodide photodissociation in its first absorption band (A band). This band is characterized by a broad featureless absorption spectrum that is formed from transitions to the $A^1\Pi$, $a^3\Pi_{0^+}$, and $a^3\Pi_1$ states. Absorption in the A band leads to prompt HI dissociation into two possible channels $H(^2S) + I(^2P°_{3/2})$, $I^*(^2P°_{1/2})$. Determination of the branching ratio for these two channels as well as of the role each state plays in the fragmentation process is of great importance not only for HI but also for a much broader class of halide molecules for which HI serves as a prototype system.

Very recently, Camden et al.[3] measured branching ratios and anisotropy parameters for the HI($v = 2$, $J = 0$) photolysis in the 297−350 nm wavelength range. On the basis of their experimental data, the authors came to a conclusion that “the new branching ratio measurements disagree with predictions obtained from the *ab initio* calculations”. They also varied parameters of the potential energy curves and transition moment functions for the A band states involved in the photodissociation to achieve the best possible agreement between theory and experiment, constructing two sets of the potential + transition moment data (models 1 and 2).

The goal of this comment is to analyze how large the discrepancy between theory and experiment in reality is, to understand its causes, and to find a way to achieve better agreement between the measured and theoretical data. Before turning to a detailed analysis of the new experimental data in comparison with theory, we shall briefly summarize the results and conclusions of our previous work.[1,2]

First of all, we have carried out multireference configuration interaction singles and doubles (MRD−CI) calculations including spin−orbit coupling for the $X^1\Sigma^+$ ground state as well as for the low-lying valence and Rydberg states.[1] The electric-dipole moments have also been computed for transitions from the ground to the A band states in the whole range of internuclear distances. A number of observations that are important for analysis of the HI photodecay have been made on this basis. For example, the $a^3\Pi_{0^+}$ state has been found to possess a shallow minimum of 600 cm^{-1} depth outside the Franck−Condon (FC) region. This means that modeling the $a^3\Pi_0{}^+$ potential curve by a single exponent, which has been a common practice before, cannot be considered as an adequate approximation. In addition, contrary to what is usually assumed, the $a^3\Pi_1$, $A^1\Pi_1 \leftarrow X0^+$ transition moments have been found to grow rapidly at shorter distances, while the $a^3\Pi_{0^+}$ transition moment has shown an opposite trend within the FC region. It has also been demonstrated that the influence of the $t^3\Sigma_1^+$ state[1] and of the nonadiabatic effects (for more details, see ref 2) on the photodissociation yields is negligible in the essential part of the A band.

Employing the above *ab initio* data, partial and total absorption spectra for the A band have been calculated and the I* quantum yields, $\Phi_{I^*}(\nu)$, determined as a function of excitation energy from the $X0^+$, $v = 0$ state. The latter quantity is also often called the branching ratio and denoted as Γ in the modern literature, and we shall use this term below in order to avoid any misunderstanding. The calculated extinction coefficients and Γ values have been found to be in good overall agreement with the experimental data, although the $\Gamma(\nu)$ function is slightly shifted to smaller excitation energies and possesses slightly higher maximum values. Possible reasons for such a discrepancy have been discussed in ref 1, and this issue will be addressed in more detail in the following.

Finally, the branching ratios for excitation from $X0^+$, $v = 1$, 2 have been calculated. It has been predicted that significantly higher I* yields (up to 0.8−0.9) may be obtained when vibrationally hot HI molecules are excited in the appropiate spectral range. This demonstrates an effective way to influence yields of the photodissociation products by changing vibrational excitation in the initial state. In the case of HI and similar molecules such as CH_3I, CF_3I, and so forth, this is of particular importance, since it allows one to influence the generation properties of these systems based on the I*/I inverse population. It should be noted that no experimental Γ values for excitation from $X0^+$, $v > 0$ were available at that time.

As already mentioned, an issue of the precision of the *ab initio* calculations has been partly addressed in ref 1. It has been noted that the computational method employed normally leads to a slight overestimation of the excitation energies of singlet states in comparison with triplets, mainly due to the difficulties in obtaining larger correlation energies for the low-multiplicity states with the same accuracy as those for their high-multiplicity counterparts. In the case of HI, a rough estimate of this effect may be obtained from the underestimation of the ground state binding energy: $25\,778 - 25\,235 = 543$ cm^{-1}. To calculate a more accurate absorption spectrum and branching ratios in HI, one has to either shift the singlet $X^1\Sigma^+$ and $A^1\Pi$ states downward or the triplet $a^3\Pi_1$ and $a^3\Pi_{0^+}$ states upward. The latter, that is, $E(a^3\Pi_{0^+,1}) + 500$ cm^{-1}, was done in ref 1. As can be seen from Figures 4 and 5 of ref 1, a significant improvement in agreement with experimental data is achieved in this way for the total absorption spectrum and in particular for the branching ratio.

It is natural to use the same correction for calculating an absorption spectrum and branching ratios for excitation from the X, $v = 2$ level. The results of this correction are shown in Figure 1. It can be seen (part a) that the A band absorption spectrum from X, $v = 2$ is fairly strongly influenced in the low-

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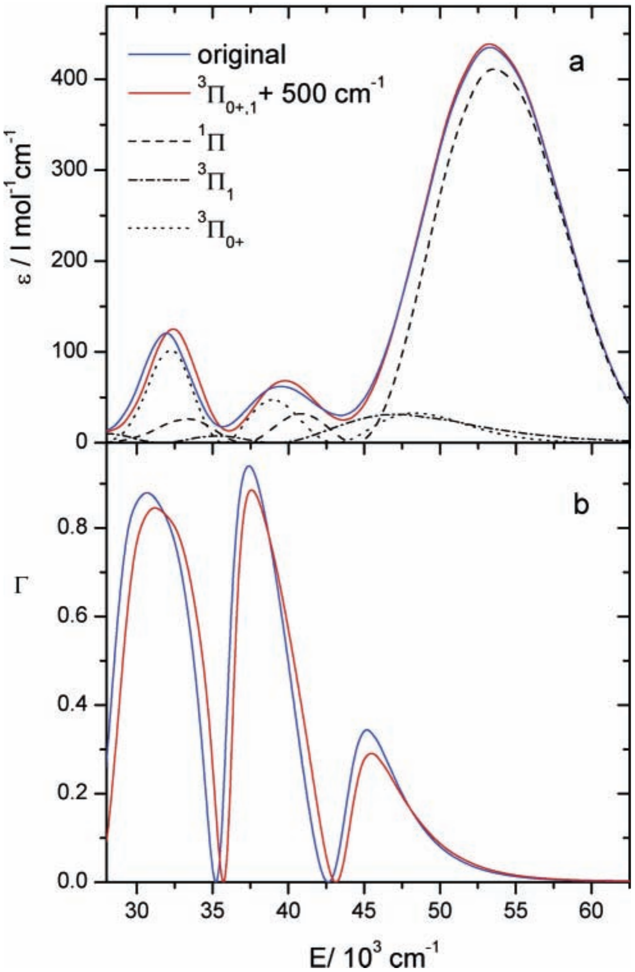

Figure 1. (a) Calculated partial absorption spectra for transitions from X0$^+$, $v = 2$ to the a$^3\Pi_1$, a$^3\Pi_{0^+}$, and A$^1\Pi_1$ states and the total absorption spectra obtained with the original computed data (blue line) and with the a$^3\Pi_{0^+,1}$ potentials shifted by +500 cm^{-1} (red line). (b) Calculated branching ratios, Γ, obtained for the original (blue) and adjusted (red) *ab initio* data for X0$^+$, $v = 2$.

energy range, while, at $E > 47 \times 10^3$ cm^{-1}, changes are minimal, since this part of the spectrum is dominated by the A$^1\Pi \leftarrow$ X transition (a small technical error made for the latter partial spectrum has been corrected in the present study). The above changes in the absorption lead to even more significant changes in the Γ values (see part b) in the corresponding energy range, revealing themselves in a shift of the Γ(ν) function to higher energies and somewhat smaller Γ values at the maximum. The excitation energy range, for which experimental measurements were done in ref 3, is magnified in Figure 2 in which the calculated branching ratios, original and corrected data, are presented in comparison with the experimental results. It can be seen that the above simple correction removes the main part of the discrepancy between theory and experiment.

As can be seen from Figure 2, it is possible that there is still a slight systematic overestimation of the Γ values remaining. This is not of decisive importance, because the present results already lie inside the experimental error bars. It is interesting, however, to understand what might be the reasons for this possible distinction. In our opinion, it may be caused by some small errors in the calculation of transition moments, most probably by a slight underestimation of the μ(A$^1\Pi \leftarrow$ X) transition moment at the CI level, as discussed in ref 1. A small increase in the strength of perpendicular transitions will lead to further improvement in the agreement between the calculated and experimental data. This point is illustrated by a dotted line in Figure 2 that corresponds to an increase in the μ(A$^1\Pi$, a$^3\Pi_1 \leftarrow$ X) values by 5% in the whole range of internuclear distance. The a$^3\Pi_1 \leftarrow$ X transition borrows its intensity mainly from A$^1\Pi \leftarrow$ X, and this explains why it should be corrected as well. As can be seen, a further improvement in agreement between the calculated and experimental Γ values is achieved, bringing them to an almost perfect match. It is also possible that the a$^3\Pi_{0^+} \leftarrow$ X transition moment has been slightly overestimated in our earlier work[1]. This is indicated by somewhat smaller μ(a$^3\Pi_{0^+} \leftarrow$ X) values obtained in test calculations carried out with larger Ω spaces in ref 1. This would lead, however, to the same change in the branching ratios as an analogous increase in the perpendicular transition moments discussed above, and thus, these two cases could be distinguished only by measuring the corresponding absorption spectrum.

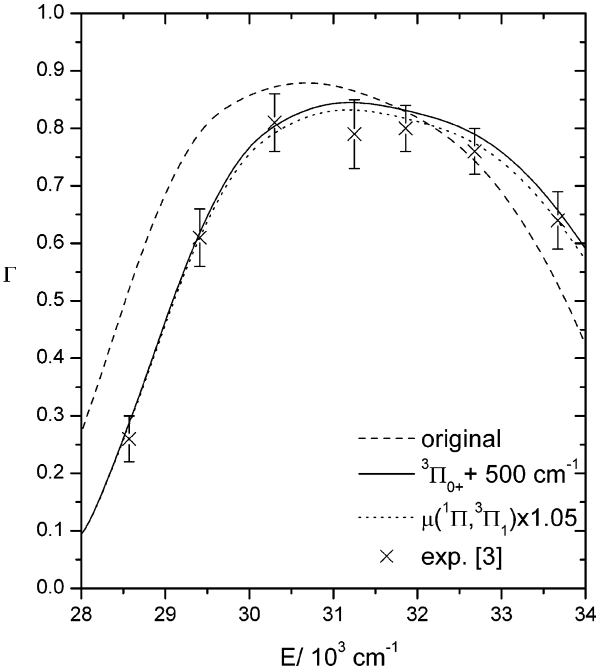

Figure 2. Calculated branching ratios, Γ, obtained for the original (dashed line) and shifted (solid line) computed data for photoexcitation from X0$^+$, $v = 2$. The dotted line represents theoretical data obtained with the a$^3\Pi_{0^+,1}$ potentials shifted by +500 cm^{-1} and the μ(A$^1\Pi$, a$^3\Pi_1$) transition moments multiplied by a factor of 1.05.

It is important to underline that the above corrections are based *not on agreement with experiment* but on the intrinsic properties of the computational method employed. If we assume that they are correct, then one comes to the conclusion that model 2 considered in ref 3 is probably unrealistic. According to this model, the $^3\Pi_1$ and $^3\Pi_{0^+}$ states should lie notably lower than the calculated potentials, which contradicts the above analysis. In addition, model 2 uses a a$^3\Pi_{0^+} \leftarrow$ X transition moment function that increases at shorter distances. All calculations that have been carried out with various reference sets and selection thresholds at the CI level as well with the varying number of roots included in the spin−orbit treatment have indicated the opposite trend. Since the relative accuracy of the calculations is normally better than absolute, it is natural to suppose that the present data reproduce the distance dependence of this transition moment correctly. These two arguments speak strongly against model 2.

It can also be noted that the authors of ref 3 came to a conclusion that the existing experimental data could not differentiate between these two models. The present analysis clearly supports model 1, but the best way to make a choice between them and also to have an additional test for the theoretical data is to measure the HI(X, $v = 2$) absorption spectrum in the (30−35) × 10^3 cm^{-1} range. Model 1 leads to almost two times stronger absorption at 32 500 cm^{-1} than model 2 (≈96 vs 58 L mol^{-1} cm^{-1}), which should help to make a decision in favor of one or the other. The corresponding ϵ value calculated from the original *ab initio* data is 112 L mol^{-1} cm^{-1} and thus much closer to the result obtained in model 1, which is characterized by relatively small changes in the calculated potentials and transition moments. The ϵ value determined with the corrected *ab initio* data is 127.3 L $\text{mol}^{-1}\text{cm}^{-1}$, and it would be very useful to check experimentally whether not only better branching ratios but also a more accurate absorption spectrum can be obtained in this way.

In summary, it can be concluded that the theoretical predictions for the HI photodissociation branching ratios agree quite well with the measured data, not only for excitation from the X, $v = 0$ level but also for $v = 2$ as well. The new experimental data[3] provide additional support for the theoretical inference made in ref 1 that the main source of error in the *ab initio* calculations lies in the underestimation of the correlation energy for the singlet states ($X^1\Sigma^+$ and $A^1\Pi$). A simple and theoretically meaninful correction, namely, a small shift of the A band triplet states to higher energies, essentially removes the discrepancy between theory and experiment. The root-mean-square discrepancy between the calculations and experiment can be further reduced by a small (5%) increase in the computed dipole moment values for the perpendicular transitions (or a similar decrease in the $\mu(a^3\Pi_{0^+} \leftarrow X)$ values), although this effect is notably weaker.

References and Notes

(1) Alekseyev, A. B.; Liebermann, H.-P.; Kokh, D. B.; Buenker, R. J. *J. Chem. Phys.* **2000**, *113* (15), 6174.

(2) Balakrishnan, N.; Alekseyev, A. B.; Buenker, R. J. *Chem. Phys. Lett*. **2001**, *341*, 594.

(3) Camden, J. P.; Bechtel, H. A.; Brown, D. J. A.; Pomerantz, A. E.; Zare, R. N.; Le Roy, R. J. *J. Phys. Chem. A* **2004**, *108* (39), 7806.