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Coriolis interaction and the division of energy between vibrational and rotational excitation induced by photoelectron recoil

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The effect of the Coriolis interaction upon the sharing of energy between rotational and vibrational excitation during an electronic transition is considered with particular emphasis on recoil-induced excitation during photoionization. If there is a large change in equilibrium bond length upon ionization, then Coriolis coupling leads to a significant transfer of energy between rotational and vibrational excitation. Experimental results for valence ionization of N_2 and CO and for carbon 1s ionization of CO show evidence of this effect.

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I. INTRODUCTION

When a photoelectron is ejected from an atom in a molecule the atom has a momentum that is equal to and opposite to the momentum of the ejected electron $p_e = k_e\hbar$. As a consequence the atom has a "recoil" kinetic energy of $p_e^2/(2m)$, where m is the mass of the atom. The molecule acquires the same momentum in the photoemission event, and, as a consequence, has a kinetic energy of $p_e^2/(2M)$, where M is the mass of the molecule. The difference between these two energies ϵ_{int} is taken up by internal rotational and vibrational excitation of the residual ion. These effects have been observed for both free molecules [1–8] and solids [9,10].

Determining how the internal energy divides between vibrational and rotational excitation (and between the various vibrational modes) is straightforward as long as the geometry of the ion is the same as the geometry of the neutral molecule. In this case, we can project the momentum of the recoiling atom onto the normal-mode vectors of the ion (in momentum space) to determine what fraction of the recoil momentum ends up in each normal mode [2]. For a diatomic molecule the procedure is quite simple; the component of momentum along the bond axis leads to vibrational excitation, and the component perpendicular to the bond axis leads to rotational excitation. If the photoelectron emission is isotropic in the molecular frame (after averaging over the angles between the polarization direction and the molecular axis), then 2/3 of the recoil energy appears as rotational excitation and 1/3 as vibrational excitation.

If, however, the equilibrium geometry of the ion is different from that of the neutral molecule, the situation is more complicated. Consider the case of emission of a carbon 1s photoelectron from CO in the direction perpendicular to the molecular axis. For simplicity assume that the initial angular momentum of the molecule is zero. Classically the recoil imparts an angular momentum to the ion that is equal to $p_e R_0$, where R_0 is the distance of the carbon atom from the center of mass of the molecule. The rotational energy associated with the recoil is, at the moment of ionization, equal to $p_e^2/(2m)$. This can also be written as $(k_e R_0)^2 B_i$, where B_i is the rotational constant of the neutral molecule [11].

The equilibrium bond length of core-ionized CO is less than that of the neutral molecule and, consequently the newly formed ion has an average vibrational energy that is equal to the excess potential energy that arises from stretching the bond from the equilibrium value for the ion to the equilibrium value for the molecule. The ion oscillates about this new bond length. At every stage of this oscillation, the bond length is shorter than that of the neutral molecule, the moment of inertia is smaller, and the rotational constant is larger. However, the angular momentum remains constant, and, consequently, the average rotational energy, equal to $(k_e R_0)^2 B_f$, is greater than the initial rotational energy. (B_f is the rotational constant of the ion at its equilibrium bond length.) The effect can be significant as can be seen from Table I where values of the rotational constants are given for several diatomic molecules and their ions.

This extra rotational energy comes from the Coriolis interaction as the bond length gets shorter. This interaction transfers energy from the vibrational mode to the rotational mode (and vice versa as the molecule oscillates from the inner turning point back to the outer turning point). As a result, the average vibrational energy is less than we would expect, and the Franck-Condon distribution of vibrational intensities is different from what we would calculate from the usual analysis.

The effect on the average vibrational excitation ΔE_{vib} can be seen by considering the vibrational potential energy for the ionized molecule $V_f(r,J)$,

$$\Delta E_{\text{vib}} = V_f(r_{e,i},J) - V_f(r_{e,f},J), \tag{1}$$

where $r_{e,i}$ and $r_{e,f}$ are the equilibrium bond lengths of the neutral and ionized molecules and J is the angular momentum quantum number. For a diatomic molecule we can set

$$V_f(r,J) = V_f(r,0) + J(J+1)\hbar^2/(2\mu r^2), \tag{2}$$

where $V_f(r,0)$ is the vibrational potential energy in the absence of any angular momentum and μ is the reduced mass. Then,

$$\begin{aligned}\Delta E_{\text{vib}} &= V_f(r_{e,i},0) - V_f(r_{e,f},0) + J(J+1)\hbar^2\big/\big(2\mu r_{e,i}^2\big)\\ &\quad - J(J+1)\hbar^2\big/\big(2\mu r_{e,f}^2\big), \qquad (3)\\ &= \Delta V_f(J=0) + J(J+1)(B_i - B_f). \qquad (4)\end{aligned}$$

Although this discussion has focused on the recoil-induced excitation, it is more general than this. If a molecule with an initial angular momentum quantum number J_0 and initial

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rotational energy $J_0(J_0+1)B_i$ undergoes a transition to a new state with the same angular momentum but with a different rotational constant B_f, then there is a change in the rotational energy from $J_0(J_0+1)B_i$ to $J_0(J_0+1)B_f$ with a corresponding modification of the vibrational energy and the Franck-Condon factors. The effect of such Coriolis coupling has been observed in a high-resolution study of photoionization of phenylacetylene [14].

The aim of this presentation is to consider several examples where the effect of the Coriolis interaction can be expected to measurably affect the division of recoil-induced internal excitation between rotational and vibrational excitation.

II. THE AVERAGE ROTATIONAL EXCITATION

In experiments aimed at investigating the recoil-induced internal excitation, the photoelectron energy is high (over 1000 eV in some cases), and it is not, in general, possible to obtain rotationally resolved spectra. Consequently it is necessary to focus on the average rotational excitation, which can be obtained from careful measurements of the positions of the centroids of peaks in a photoelectron spectrum measured relative to a suitable standard [4,5].

Starting with a classical model it can be shown [6] that the average rotational excitation energy $\langle \Delta E_{\rm rot}\rangle$, is given by the equation,

$$\langle \Delta E_{rot}\rangle = \frac{2}{3}\frac{p_e^2 R_0^2}{2I_f} + \frac{p_\omega^2}{2I_i}\left(\frac{I_i - I_f}{I_f}\right), \tag{5}$$

where p_ω is the initial angular momentum of the molecule and I_i and I_f are the moments of inertia of the initial and final molecules [15]. The factor of 2/3 arises from averaging over all directions of emission of the electron assuming that this is isotropic. The factor will be different if the distribution is not isotropic. Equation (5) can be rewritten in terms of the rotational constants as

$$\langle \Delta E_{rot}\rangle = (2/3)(k_e R_0)^2 B_f + L^2 B_f\left(\frac{B_f - B_i}{B_f}\right), \tag{6}$$

where $L = p_\omega/\hbar$. The quantum-mechanical version of this equation is

$$\langle \Delta E_{rot}\rangle = (2/3)(k_e R_0)^2 B_f + J_0(J_0+1)B_i\left(\frac{B_f - B_i}{B_i}\right), \tag{7}$$

where J_0 is the quantum number designating the initial angular momentum of the neutral molecule.

The second term in Eqs. (5)–(7) represents the effect of the initial angular momentum on the rotational energy. It is present even at low photoelectron energies where the recoil effect is negligible but is independent of the photoelectron energy. It can be either positive or negative depending on the sign of the change in bond length upon ionization. As can be seen from Table I, typical values of the fraction $(B_f - B_i)/B_i$ are a few percent (except for H_2 where the difference is quite significant). The quantity $J_0(J_0+1)B_i$ is the rotational energy of the initial molecule. In the high-temperature limit (room temperature for many molecules) the average rotational energy is $k_B T$ or 26 meV at room temperature. Thus, for core ionization of CO, for example, we can expect the second term of Eqs. (5)–(7) to be about +3 meV. This additional energy is, as has been indicated, acquired via Coriolis interaction at the expense the vibrational excitation. In the case of core ionization of CO, the average vibrational excitation is about 180 meV, which is large compared with the Coriolis-mediated energy transfer of about 3 eV. Although this should affect the Franck-Condon factors, other effects have a much greater influence on these factors at energies close to threshold [13].

TABLE I. Rotational constants (in cm^{-1}) for several diatomic molecules and their ions. Data for neutral molecules and valence ionic states are from Huber and Herzberg [12]. The datum for core-ionized CO is calculated from the bond-length change given by Kukk *et al.* [13].

Molecule	Ionic state	B_i	B_f	Ratio B_f/B_i
CO	C 1*s*	1.691	1.852	1.095
CO	Valence *X*	1.931	1.977	1.024
CO	Valence *A*		1.589	0.823
CO	Valence *B*		1.799	0.932
N_2	Valence *X*	1.998	1.932	0.967
N_2	Valence *A*		1.744	0.873
N_2	Valence *B*		2.075	1.038
H_2	*X*	60.85	30.21	0.496

The first term in Eqs. (5)–(7) represents the effect of the recoil momentum on the rotational excitation. It is independent of the initial angular momentum and increases linearly with the photoelectron energy. We can rewrite this expression as

$$\frac{2}{3}\epsilon_{\rm int}\frac{B_f}{B_i}, \tag{8}$$

where $\epsilon_{\rm int}$ is, as noted in the opening paragraph, the share of the recoil energy that goes to internal excitation. For core ionization of CO at a photon energy 2000 eV above threshold, as an example, the quantity $\frac{2}{3}\epsilon_{\rm int}$ is 35 meV. The additional rotational excitation due to the Coriolis coupling is about 10% of this and should, in principle, lead to a noticeably higher rotational excitation than would be predicted in the absence of this coupling. Since this additional energy comes at the expense of the vibrational excitation, this recoil-induced effect should be reflected in the Franck-Condon factors and how these factors vary with photoelectron energy. Thus we expect that the recoil-induced rotational excitation energy will increase more rapidly (and the vibrational excitation will increase less rapidly) than would be predicted by a model that does not include this coupling.

Several examples of recoil-induced vibrational and rotational excitation in diatomic molecules have been previously described [4,5,8,13]. These have included rotational excitation accompanying valence ionization of N_2 and CO and vibrational excitation accompanying carbon 1*s* ionization of CO. For N_2 and CO the recoil-induced rotational excitation is observed to increase linearly with the photoelectron energy as expected [4,5,8], but the rates of increase do not agree exactly with the predictions of a model that ignores the Coriolis coupling. For carbon 1*s* ionization of CO [8,13] at high photon energies the vibrational excitation appears to be less than expected. These examples are considered in more detail below.

III. EXPERIMENTAL OBSERVATIONS OF RECOIL-INDUCED INTERNAL EXCITATION

A. Rotational excitation in the valence ionization of N_2 and CO

For valence ionization of N_2 and CO to form the X, A, and B states of the ions, experimental results have been presented for recoil-induced rotational excitation, and these have been compared with theoretical predictions [4,5]. As mentioned above, there is approximate, but not perfect, agreement between the experimental results and the predictions, which do not include the effect of Coriolis interaction.

For ionization to form the B state of ${N_2}^+$, the average recoil-induced rotational excitation is found experimentally to be equal to $(1.40 \pm 0.08) \times 10^{-5}$ times the photoelectron kinetic energy. The ionized electron is expected to be predominantly a $2s$ electron, and the predicted slope for such an electron is 1.31×10^5 (in the absence of Coriolis coupling) [5], which disagrees with the observed value by slightly more than the quoted uncertainty. From Table I, we see that a correction of +3.8% must be made to the predicted value for Coriolis coupling, bringing the predicted value to 1.36×10^5, which agrees with the experimental value within the uncertainty.

For the A state of ${N_2}^+$, the ionized electron is a $2p$ electron, and the predicted slope is 1.57×10^{-5}, which is significantly greater than the observed slope of $(1.40 \pm 0.12) \times 10^{-5}$ [5]. This electron is, however, a bonding electron, with the consequence that its removal causes a large increase in the bond length and a corresponding decrease in the rotational constant. From Table I, we see that a Coriolis correction of -13% must be made to the predicted value, which now becomes 1.37×10^{-5}, in satisfactory agreement with the observed value.

For the X state of ${N_2}^+$, the orbital from which the electron is ionized is a nonbonding hybrid of nitrogen $2s$ and $2p$ atomic orbitals, and the predicted slope depends critically on the degree of mixing between these [5]. It is, therefore, impossible to say whether or not the Coriolis correction, which is small in this case, plays an important role.

For the A state of CO^+ the ionized electron comes from an orbital that is a mixture of carbon $2p_\pi$ and oxygen $2p_\pi$ with the dominant contributor being the oxygen $2p_\pi$ [5]. The predicted slope for such an orbital is 1.18×10^{-5}, which is significantly higher than the observed slope of $(0.77 \pm 0.14) \times 10^{-5}$ [5]. From Table I we see that the Coriolis correction for this state of CO is -18%, leading to a corrected prediction of 0.97×10^{-5}. Although the Coriolis correction brings the predicted value closer to the observed value, the predicted value still differs from the experimental one by slightly more than the uncertainty.

For the B state of CO^+ the ionized orbital is a mixture of oxygen $2s$, oxygen $2p_\sigma$, carbon $2s$, and carbon $2p_\sigma$. Thomas *et al.* [5] considered various possibilities for this mixing and, from these, suggested a predicted slope of 1.17×10^{-5}, which is much greater than the observed slope of $(0.73 \pm 0.13) \times 10^{-5}$. The Coriolis correction reduces the prediction to 1.09×10^{-5}, which is still far from the measured value. Thomas *et al.* concluded that it is difficult to match theory and prediction with any reasonable assumption about the orbital mixing, and even with the Coriolis correction, this conclusion remains.

Predictions for the X state of CO^+, which arises from ionization of an orbital that is primarily carbon $2s$, range from 1.59×10^{-5} to 1.74×10^{-5} [5], both significantly greater than the observed value of $(1.35 \pm 0.07) \times 10^{-5}$. Including the Coriolis correction, which is positive but small, does not improve this agreement.

Summarizing the results for valence ionization of N_2 and CO, we see that for the A and B states the Coriolis correction leads to predictions that are in better agreement with the experimental results. With this correction the predicted slopes for N_2 are within the uncertainties of the experimental values, and those for CO are in better agreement with the experimental values than are the uncorrected predictions. For the X state in N_2 no conclusion is possible. For the X state in CO the Coriolis correction is in the wrong direction to bring the prediction into better agreement with the measurement but is small.

It is to be noted that the predictions are based on simplified approximations for the molecular-frame photoelectron angular distributions (MFPADs), namely, that these will be isotropic for s electrons and will go as $\cos^2\theta$ for p_σ electrons and as $\sin^2\theta$ for p_π electrons [5,16]. If the MFPADs differ from these, then the predictions must be modified accordingly.

B. Vibrational excitation in the carbon 1s ionization of CO

As noted in the Introduction, for isotropic emission of a photoelectron from a diatomic molecule two-thirds of the recoil-induced internal excitation goes into rotation, and one-third goes into vibrational excitation. For CO this assumption leads to a vibrational excitation $E_{\text{vib}} = (8.71 \times 10^{-6})\epsilon_e$, where ϵ_e is the kinetic energy of the photoelectron. This vibrational excitation is reflected in the Franck-Condon profile, and, in particular, in the ratio of the intensities for populating the $v = 1$ and $v = 0$ states, referred to as the "v ratio." To a good approximation, this ratio times the characteristic vibrational frequency is equal to the average recoil-induced vibrational excitation [2,8,17]. Taking the characteristic vibrational frequency of carbon $1s$ ionized CO to be 302 meV [13] leads to the relationship v ratio $= (2.88 \times 10^{-5})\epsilon_e$, where ϵ_e is given in eV.

These conclusions must be modified by the Coriolis correction. We see from Table I that this correction will be 9.5% for the rotational excitation. What the rotational excitation gains from the Coriolis interaction the vibrational excitation loses. However, the vibrational excitation is expected to be only half of the rotational excitation with the result that the Coriolis correction to the vibrational excitation reduces it by 19%.

In addition to the recoil-induced vibrational excitation there is the normal Franck-Condon vibrational excitation, which arises because the equilibrium bond length of the core-ionized molecule is about 5% less than the bond length of the neutral molecule. This leads to a v ratio of about 0.6 even if there is no recoil-induced vibrational excitation. The two effects are independent of one another and are expected to be additive [17]. In this simple approximation, a plot of the v ratio versus the electron kinetic energy should be linear with an intercept that corresponds to the Franck-Condon value and

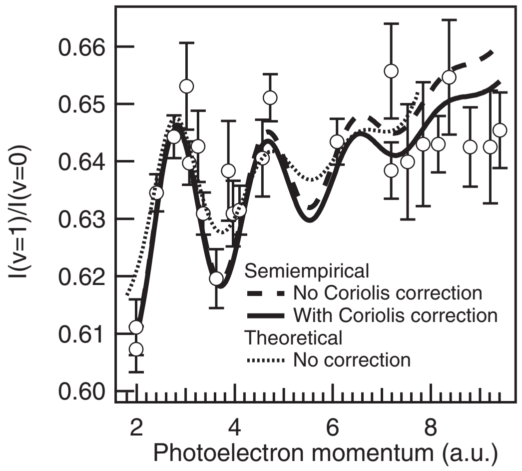

FIG. 1. Intensity ratios $(v = 1)/(v = 0)$ for carbon 1*s* ionization of CO plotted against the momentum of the photoelectron. Open circles represent the experimental data from Ref. [13]. The dashed line represents a semiempirical fit to the data, and the dotted curve represents a theoretical calculation of the ratios [13]. For both curves there has been no correction for the Coriolis interaction. The solid curve shows the semiempirical fit with inclusion of the Coriolis correction.

a slope that reflects the recoil-induced excitation. In addition, however, the energy dependence of the v ratio is modulated by shape resonance effects and interference arising from the scattering of the carbon 1*s* photoelectron from the oxygen atom [13].

These various effects have been considered in some detail by Kukk *et al.* [13], who have presented comparisons of theoretical calculations of the v ratio in CO with experimental measurements of this quantity. Some of their results are shown in Fig. 1 where the v ratio is plotted against the momentum of the photoelectron. In this figure, the open circles represent the experimental data, the dashed line shows a semiempirical fit to the data, and the dotted line shows a theoretical calculation of the ratios. For the dashed and dotted lines, the effect of the Coriolis interaction has not been included. We see that there is good agreement between theory and experiment from near threshold to a momentum of about 6 a.u. (500 eV above threshold). Beyond this energy, however, the experimental results give lower values of the v ratio than predicted, and at photoelectron energies of about 1000 eV ($k \approx 8.5$ a.u.), the discrepancy is significant. So far no satisfactory explanation has been given for this discrepancy, but it is in the direction that would be expected from the neglect of the Coriolis correction in the theoretical treatment. The solid curve shows the semiempirical curve corrected for the Coriolis interaction, and we see that this gives improved, although not perfect, agreement between the prediction and the observation. In detail the three experimental points at highest energy fall about 0.017 below the the theoretical prediction for the v ratio if there is no correction for the Coriolis interaction. Correcting for the Coriolis interaction reduces the prediction by 0.006, removing slightly more than one-third of the discrepancy and putting the prediction at the outer edge of the error bars.

It appears that including the Coriolis correction improves the agreement between prediction and observation. However, the experimental data have large uncertainties, and additional data are needed. Experiments to extend the range of the measurements to photon energies of a few keV are scheduled.

IV. SUMMARY AND CONCLUSIONS

If there is a significant change in the equilibrium bond length upon excitation or ionization, then Coriolis coupling leads to a transfer of energy between rotational excitation and vibrational excitation. The direction of the transfer depends upon the sign of the change in bond length. For ionization there are two independent contributions. One depends on the initial angular momentum of the ionized species but not on the energy of the outgoing electron. This effect is small, and it is difficult to observe in rotationally unresolved spectra or in the presence of significant Franck-Condon excitation of vibrational structure. The second contribution is independent of the initial angular momentum but is dependent on the energy of the outgoing electron. This effect is also small, but it can be recognized by the energy dependence of the apparent ionization energy in rotationally unresolved spectra or in the $(v = 1)/(v = 0)$ ratio in vibrationally resolved spectra.

For recoil-induced rotational excitation of the *A* and *B* states of N_2^+ and CO^+, inclusion of a Coriolis correction improves the agreement between the predicted and the observed energy dependence of the apparent ionization energy. This is especially the case for N_2^+ where the Coriolis correction accounts well for the apparent discrepancy between prediction and experiment. For the *X* state in both N_2^+ and CO^+ the emitted electron comes from a nonbonding orbital. As a consequence, there is only a small change in equilibrium bond length upon ionization, and consequently the Coriolis correction is small -2 to 3%. This, together with uncertainty about the atomic orbital composition of the *X* state makes it difficult to conclude that there is a Coriolis contribution in these cases.

For carbon 1*s* ionization, there is an apparent discrepancy between the predicted and the observed values of the $(v = 1)/(v = 0)$ ratio in the direction expected if the predicted values do not include the Coriolis interaction. Including this interaction removes part, but not all, of the discrepancy. The uncertainties in the experimental data are not small, and it remains to be seen in future (planned) experiments at much higher photoelectron energies how well the traditional theoretical models combined with the Coriolis correction will account for the observed results.

The experimental results discussed here involve photoelectron kinetic energies of less than about 1200 eV, and, consequently, the recoil-induced excitations are small and at the edge of detectability. It has now become possible to measure gas-phase photoelectron spectra of small molecules at kinetic energies of 6–8 keV. Since both the recoil-induced excitations and the Coriolis contribution to them increase linearly with the photoelectron kinetic energy, we can expect these effects to make significant contributions to spectra measured at these energies.

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