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EXPERIMENTAL STUDIES OF METASTABLE AND DISSOCIATIVE STATES OF DOUBLY-CHARGED MOLECULAR IONS

D. MATHUR and C. BADRINATHAN

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India

RESUME: La spectrométrie haute résolution par perte d'énergie translationnelle a été appliquée à l'étude des produits des collisions à perte d'électrons et des collisions à double capture d'électrons conduisant à la formation d'ions moléculaires doublement chargés. Un cas d'étude a été reporté sur les états electroniques des ions CO$_2^{2+}$ métastables à énergie, la plus basse et instables. Nos données expérimentales sont utilisées pour vérifier la vérité des derniers calculs sur les courbes d'énergie potentielles de CO$_2^{2+}$, utilisant des techniques SCF relativement directes, telles que MNDO, comme un nombre de méthodes d'ab initio orbitales moléculaires à haut niveau.

ABSTRACT: High resolution ion translational energy loss spectrometry has been applied to study products of electron-loss collisions and double electron capture collisions leading to formation of doubly charged molecular ions. A case study is reported on the lowest-energy metastable and unstable electronic states of CO$_2^{2+}$ ions. Our experimental data is utilised to assess the reliability of recent calculations of CO$_2^{2+}$ potential energy curves using relatively straightforward SCF techniques, such as MNDO, as well as a number of high-level ab initio molecular orbital methods.

INTRODUCTION

Quantum chemical information on diabatic and adiabatic potential energy surfaces of a new class of molecular species - multiply charged molecular ions of the type AB$_q^+$ - is not only of intrinsic, fundamental interest but also provides critically important input for high-level quantal calculations of cross sections for electron capture by multiply charged atomic ions, A$_q^+$, from neutral species, B. Theoretical evidence indicates that such cross sections are extremely sensitive to the electronic energy level structure of AB$_q^+$ ions. The prediction of such energy levels within single-channel descriptions afforded by the Born approximation is generally inadequate due to the fact that theoretical generation of quantitatively-reliable potential energy functions for species of the type AB$_q^+$ is considerably more complex than for singly charged AB$^+$ or neutral AB. The additional complexity arises from perturbations due to multiple avoided curve-crossings that can occur between attractive diabatic states of the type A$^+$B and repulsive, Coulombic states A$(q-1)^+ B^+$. It is the formation of potential energy barriers due to such avoided curve-crossings that leads to the metastability of multiply charged molecular species such as AB$_q^+$.

Of course, not every avoided crossing gives rise to a significantly deep potential barrier. Consider, as an illustration, the case of a doubly charged diatomic such as CH$_2^2$. Whether or not a metastable electronic state arises out of the avoided crossing between the attractive C$_2^+$-H$^+$ potential energy curve and the strongly repulsive C$^+_t$-H$^+$ curve depends on the orientation of the ps orbital in C$_t$($^2P$) with respect to the C$^+_t$-H$^+$ internuclear axis. In fact, it is the overlap of the ps electron with the is orbital of H$^+$ that determines the stability of the CH$_2^2$ bond; an orientation along the C$^+_t$-H$^+$

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axis results in formation of metastable \( 2^\Sigma \) states whereas an orientation perpendicular to the internuclear axis gives rise to purely dissociative \( 2^\Pi \) states.

It is clear that experimental information on the energetics of multiply charged molecular ion formation processes is of considerable importance in assessing the effectiveness of various contemporary quantal techniques of calculating potential energy functions of such molecular species. In this paper we focus attention on ion translational energy spectrometry experiments that yield quantitative energetics information on processes governing the formation of metastable as well as dissociative electronic states of doubly charged molecules. A case study of low-lying states of \( \text{CO}^{2+} \) ions is presented.

**EXPERIMENTAL METHOD**

A schematic diagram of an apparatus which enables two distinct types of ion translational energy spectrometry experiments to be conducted is shown in fig. 1.

In the case of ion-neutral collisions leading to electron-loss (charge stripping), the experimental method involves the formation of singly charged \( \text{CO}^+ \) ions in the low voltage arc type of ion source. Such ions are extracted at an accelerating potential in the 3-5 kV range, and are focussed on the entrance plane of a Wien filter which carries out charge/mass analysis by means of crossed electric and magnetic fields. The mass-selected ions pass through a collision cell containing a low pressure gas, such as He or Ar, and thence to a high resolution electrostatic energy analyser which determines the energy defect, \( \Delta E \), in the kinetic energy spectrum of product \( \text{CO}^{2+} \) ions resulting from a charge stripping collision of the type

\[
\text{CO}^+ + \text{He} \rightarrow \text{CO}^{2+} + \text{He} + e^+ - \Delta E
\]  

Accurate determination of the minimum energy defect, \( \Delta E_{\text{min}} \), for process (1) yields the ionisation energy of \( \text{CO}^+ \) ions and, hence, the double ionisation energy of \( \text{CO} \).

In the case of ion-neutral collisions leading to double electron capture, the projectile ion is generally chosen to be 'structureless', such as \( \text{H}^+ \), and the collision investigated is of the type

\[
\text{H}^+ + \text{CO} \rightarrow \text{H}^+ + \text{CO}^{2+} - \Delta E
\]  

Measurement of the energy defect and knowledge of the ionisation energy and electron affinity of the projectile species enables determination of the double ionisation energy of the target molecule.

The real significance of carrying out both types of translational energy spectrometry experiments lies in the fact that different electronic states of the doubly charged molecule may be accessed in each experimental situation, within a signal apparatus. The
nature of the electron loss experiment requires the measured $\text{CO}^{2+}$ ion single to be due to a metastable state of the doubly charged molecule whose lifetime must have a lower limit which is at least equal to the transit time for the ion to traverse the distance between the collision cell and the ion detector. In the experimental configuration shown in fig. 1, for collision energies of the order of 3 keV, this transit time is ca 3 μs. The metastable state accessed in such charge stripping experiments need not be the lowest energy state.

In constrast, the double electron capture technique does not impose any lifetime constant on the $\text{CO}^{2+}$ state being accessed. As it is the product negative ion that is actually detected, and not the doubly charged ion, this technique yields double ionisation energies of molecular species independently of the stability of the ionic species towards dissociation. In this respect, data obtained by this method complements that available from Auger spectroscopy experiments. Cross sections for double electron capture collisions can be surprisingly large\(^3\). Various constraints imposed by symmetry and spin selection rules can, usually, be overcome by suitable choice of projectile species which must possess reasonably large, positive values of electron affinity. F\(^+\), Cl\(^+\), OH\(^+\) and O\(^+\) are examples of projectile ions used in recent experiments.

RESULTS AND DISCUSSION

Typical high resolution translational energy spectra of product ions from electron loss collisions (eqn. 1) and double electron capture collisions (eqn. 2) are shown in figs. 2 and 3, respectively. Experimental details of energy calibration and ion identification procedures have been presented in an earlier report\(^2\).

In the case of electron loss collisions, the mean minimum energy defect for reaction (1) has been measured to be $26.20 \pm 0.35$ eV. This value represents the vertical single ionisation energy of $\text{CO}^+$ ions. Adding to it the ionisation energy of CO determined by uv spectroscopy ($14.013$ eV) yields a value of $40.21 \pm 0.35$ eV for the double ionisation energy pertaining to the lowest metastable state of $\text{CO}^{2+}$.

![Image of energy spectra](image-url)

**Fig. 2:** a) Inelastic and b) elastic peaks obtained in 3 keV charge stripping collisions of $\text{CO}^+$ with He.
Fig. 3 shows the $\text{H}^-$ translational energy spectrum resulting from double electron capture reactions. Two relatively sharp peaks, marked A and B, are clearly observed. The former results from a single collision between $\text{H}^+$ and CO of the type indicated in reaction (2). B, on the other hand, only manifests itself at high collision cell gas pressure, when double collisions of the type

$$\text{H}^+ + \text{CO} \rightarrow \text{H} + \text{CO}^+$$
$$\text{H} + \text{CO} \rightarrow \text{H}^- + \text{CO}^+$$

occur to yield a negative ion product. As has been shown previously$^2$, measurement of the energy separation between peaks A and B enables determination of the onset energy for formation of $\text{CO}^{2+}$ in its lowest energy state. The present data yields a value of $39.45 \pm 0.20$ eV for this energy.

The two values of double ionisation energy may be correlated with different electronic states of $\text{CO}^{2+}$. The fact that metastable $\text{CO}^{2+}$ states do exist can readily be established by simple molecular orbital calculations. Fig. 4 shows the result of one such calculation, using the relatively straightforward SCF technique MNDO, of potential energy curves for $\text{CO}$, $\text{CO}^+$ and $\text{CO}^{2+}$. The vertical ionisation energy of $\text{CO}^{2+}$ is deduced to be $13.90$ eV, which compares reasonably well with the experimental value of $14.01$ eV established by photoelectron spectroscopy. The potential energy function for $\text{CO}^{2+}$ shows a well deep enough to maintain several vibrational levels; the double ionisation energy is deduced from fig. 4 to be $39$ eV. Underestimation of these calculated values is a consequence of the difference in the number of valence electrons between CO, CO$^+$ and CO$^{2+}$; this difference results in successively smaller contribution of electron correlation for the electron-deficient species. The value of the equilibrium internuclear distance obtained for the computed metastable $\text{CO}^{2+}$ state is $1.2\text{Å}$, in good accord with the value obtained in much more sophisticated calculations (see below).

A similarly shaped $\text{CO}^{2+}$ potential energy curve is obtained in more rigorous calculations. Fig. 5 shows the results of our $\text{a}^\text{b initio}$ spin-restricted Hartree-Fock molecular orbital calculations using STO-3G basis functions for both carbon and oxygen. A potential
well is again observed for the $^{3}\Pi$ state of CO$^{2+}$; the vertical double ionisation energy for this state is computed to be 40 eV.

The CO$^{2+}$ ion has attracted considerable quantum chemical interest recently. In fig. 6 we depict the potential energy curves for low-lying electronic states of the doubly charged molecule calculated using various sophisticated, state-of-the-art ab initio quantal techniques. The calculated curves of Wetmore et al indicate surprisingly deep potential minima (depths of the order of 2 eV) for all the low-lying singlet and triplet states. These large depths are not reproduced in the other calculated curves (fig. 6b, c). Moreover, whereas rapid predissociation of the $^{1,3}\Pi$ states

![Graph 1](image1)

**Fig. 4:** MNDO potential energy curves for CO, CO$^+$ and CO$^{2+}$.

![Graph 2](image2)

**Fig. 5:** ab initio potential energy curves for CO, CO$^+$ and CO$^{2+}$ using a STO-3G basis set.

by the $^{3}\Sigma^-$ state would be expected from the curves shown in fig. 6a, the calculations of Olsson and coworkers (fig. 6c) indicate that several vibrational levels of the lowest $\Pi$ state would be stable. This is also in conformity with the expections from the potential energy curves of Mazumdar et al (fig. 6b). The latter set of curves indicates a metastable $^{3}\Pi$ state (at least for the lowest vibrational level) and an unstable $^{1}\Pi$ state whose $v = 0$ level is predissociated by the purely repulsive $^{3}\Sigma^-$ curve.
Fig. 6a: PE curves for low-lying states of doubly charged CO calculated by Wetmore et al (ref. 4)

Fig. 6b: PE curves for low-lying states of doubly charged CO calculated by Mazumdar et al (ref. 2)

Fig. 6c: CASSCF PE-curves for triplet states of doubly charged CO (unpublished data from Olsson et al (ref. 5))
Comparing experimental and theoretical information, it is possible to ascribe the measured ionisation energy of 40.21 eV to the lowest $\Omega^3{^1}\Sigma^+_{\Pi}$ state of CO$^{2+}$ whose potential curve, according to the calculations of Mazumdar et al., has an equilibrium C-O distance of 1.2 Å and a potential well which is deep enough (0.9 eV) to support a number of vibrational levels. The other measured value of 39.45 eV is ascribable to the lowest $\Omega^3{^1}\Sigma^+_{\Pi}$ state whose potential curve is unlikely to support even a single vibrational level due to a curve crossing with the $\Omega^3{^1}\Sigma^-$ state. The energy difference of 0.64 eV between the two measured values may be a measure of singlet-triplet splitting.

In the light of the experimental data and its relationship to theoretical information, it is possible to seek explanations for the differences in various calculations. For instance, it becomes possible to suggest that the orbitals used in the configuration interaction calculations of Wetmore et al., which were obtained from restricted Hartree-Fock (HF) calculations for the $\Omega^3{^1}\Sigma^+$ state, may deviate considerably from those obtained using 'unrestricted HF procedures in which spin polarisation effects on the shapes of the orbitals are more appropriately considered. Such polarisation effects should be particularly significant for internuclear distances $r_\text{e}$ larger than 1.13 Å ($r_\text{e}$ for neutral CO). This may also partially explain the rather large values of potential barriers in fig. 6a.

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