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Synchrotron radiation induced photoionization and photodissociation of small molecules

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Tunable synchrotron radiation makes possible detailed studies of molecular photoionization and photodissociation. This is particular true if the induced reactions may be studied in various decay channels such as formed ions and positive and negative fragments as well as fluorescence in different wavelength regions. We have performed studies of this kind in the low energy range (14 - 35 eV) using the Swedish synchrotron facility MAX in Lund. A special detection channel has been constructed for the purpose involving two sections, one low pressure chamber with a quadrupole mass spectrometer and one high pressure chamber for fluorescence detection using a variety of photomultipliers. The studies performed so far involve small fundamental molecules such as N_2 [1,2], O_2 [3,4], CO [5] and NO [6] as well as CO_2 [7], methane[8] and neopentane[9]. While a great number of the observed lines are already known, several strong lines and series have been classified for the first time. The combination of information from the mass spectra and the fluorescence spectra contribute important information concerning autoionization and predissociation of the involved Rydberg states.

1. DETECTION OF MASS SPECTRA AND FLUORESCENCE

The general experimental situation is sketched in Fig.1 in the case of the single ionization region in the vicinity of the first ionization potential (I.P.). At a given energy $(h\nu)_{exc}(\geq \text{I.P.})$ of the exciting synchrotron light a molecule, AB, will dissociate or will be ionized either via a direct process or via a "doorway" Rydberg state $(AB)^*$. In practice the latter process will frequently be far more important and will give rise to a rich line structure in the measured mass spectra $(AB)^+$, A^+ or fluorescence spectra according to the scheme shown in Fig.1. More specifically $(AB)^+$ ions are formed in autoionization of $(AB)^*$, while A^+ fragments are formed in predissociation either into $A^+ + B^*$ or ion pairs $A^+ + B^-$. Fluorescence photons may be emitted from the molecule $(AB)^+$ (IR, visible, UV) as well as from excited fragments (generally UV radiation). The combined information from all these decay channels gives a detailed information about photoionization and photodissociation of molecules as well as about the level structure in the single ionization region.

Fig.1 Basic processes in photoionization and photodissociation. Ionization and dissociation may either take place through a direct process or via a autoionization or predissociation via "doorway" Rydberg state $(AB)^$. The direct and indirect processes may be studied using various detection channels such as the formed ions $(AB)^{+*}$, $A^\pm$, $B^\pm$ or fluorescence from the molecules $(AB)^{+*}$ or the atoms B^* and A^* . Interferences between the direct and indirect processes give rise to Fano profiles and the doorway states appear as a discrete structure in all detection channels.*

Fig.2 Experimental arrangement for detection of ions, ion fragments and fluorescence from synchrotron radiation induced photoionization and photodissociation of free molecules (from ref.[4]).

2. EXPERIMENTAL

Fig.2 shows our equipment for studies of this kind at the Swedish synchrotron facility MAX in Lund. Dispersed light (10 - 40 eV) from a 1m normal incidence monochromator enters a mass analysis chamber (ambient pressure ≤ 0.01 mTorr) where the ions and ion fragments are formed from an effusive jet and pushed towards a quadrupole mass spectrometer (QMS) by an electrostatic repeller. A second "high pressure" chamber is attached to the QMS chamber via a capillary, where the fluorescence from a second jet is focussed and detected with various PM tubes for different wavelengths. The total synchrotron flux was continuously monitored using a calibrated silicon diode.

3. EXAMPLES OF MOLECULES STUDIED AT MAX

3.1 Oxygen

Fig.3 shows the $(c^4\Sigma_u^-)3s\sigma_g$ $v'=0,1$ Fano "window" resonances in O_2 viewed by detection of O_2^+ ions (a), 5300 - 6500 Å fluorescence (b), O^+ ions (c), 1150 - 3200 Å fluorescence (d), 1150 - 2000 Å fluorescence (e). A lot of information can be gleaned from this set of curves. Thus, (c) and (e) represent dissociation into $O^* + O^+$ and $O^* + O(^*)$ fragments, respectively, and these curves are mutually different and also different from the remaining curves. The explanation follows from the shallow potential curve of the $(c^4\Sigma_u^-)3s\sigma_g$ state which only supports the $v'=0$ and the $v'=1$ levels. No molecular emission from the latter level occurs in view of rapid tunneling through the barrier, while the $v'=0$ level preferably decays by $c \rightarrow b$ emission (1940 - 2360 Å). Thus,

the $v' = 1$ emission peak in curve (e) stems from excited O^* dissociation fragments ($\lambda = 1302 - 1304 \text{ \AA}$ multiplet) while the broad peak to the left of the $v' = 1$ peak follows from direct dissociation to the repulsive part of the c-potential curve.

3.2 Nitrogen

Molecular nitrogen has been exposed to synchrotron light in the range 16 - 40 eV and the N^+ , N_2^+ mass spectra have been studied [1] as well as the fluorescence [2]. Line structures are observed which are interpreted in terms of autoionization or dissociation of well known Rydberg states in N_2 converging to the B, C and D states in N_2^+ . In addition a new member of the Rydberg series converging to the D state is found.

Fig.3 The Fano resonances $O_2(c^4\Sigma_u^-) 3s\sigma_g$, $v' = 0,1$ viewed in different detection channels. (a): O_2^+ ions, (b): fluorescence 5300 - 6500 Å, (c): O^+ ions, (d): fluorescence 1150 - 3200 Å, (e): fluorescence 1150 - 2000 Å. Peak A in curve (e) probably follows from direct bound-free dissociation from the O_2 ground state to the left continuum part of the $(c^4\Sigma_u^-) 3s\sigma_g$ potential curve (from ref[4]).

Fig.4 Production of $^{12}CO^+$ and $^{13}CO^+$ ions at bombardement of natural CO gas with 860 - 890 Å photons. The strongest transitions in the $^{12}CO^+$ spectrum have hitherto been unclassified, but the isotope shifts observed above suggest that they form the lowest ($n = 9$) vibrational progression of the R_A series (from ref[5]).

3.3 Carbon monoxide

The decay products of CO were studied in various detection channels such as formed CO^+ and C^+ ions and visible or VUV fluorescence. A rich line structure is observed which are attributed to CO Rydberg series converging to the X, A, B, D, C and E states in CO^+ . While a great number of these lines are already known, some of them are classified here for the first time such as the R_A ($n = 3$) progression which has been discovered from comparisons of the $^{12}CO^+$ and $^{13}CO^+$ spectra (Fig.4)

3.4 Nitric oxide

Studies of the photoion excitation (PIE) spectra of NO^+ , N^+ , O^+ and O^- formed from NO at MAX [6] have yielded extended information about the structure of Rydberg series converging to all known states in NO^+ below 24 eV and their interactions with other states. Several predissociations have been found caused by a number of NO^+ states as well as NO ion pair states.

3.5 Polyatomic molecules

Among the studied species could here be mentioned carbon dioxide[7], methane[8] and neopentane[9]. In the case of CO_2 the combined information from the PIE spectra of CO_2^+ , CO^+ , O^+ and C^+ as well as visible and VUV fluorescence have been used for classifications of Rydberg series converging to the X, A, B and C states in CO_2^+ . A transition to a bent valence state has been recorded and discussed. Neopentane is a well-known example of a high-symmetry molecule where our PIE spectrum shows a broad shape resonance around 16 eV which decays preferentially through the $3t_2^{-1}$ ionization channel.

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