VACUUM-ULTRAVIOLET ABSORPTION SPECTRA OF SMALL MOLECULES IN THE SOLID PHASE

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A synchrotron that provides intense and energetic radiation with a continuous span enables quantitative measurements of both wavelength or wavenumber and intensity in the vacuum-ultraviolet region for compounds of astrophysical interest. We present absorption spectra of CO, CO_2, H_3COH, N_2O, O_2 and NO in solid phases at 10 K to show the quality of spectra that is achievable with a cryogenic refrigerator coupled to a beam line of the Taiwan synchrotron producing radiation in a region of wavelength greater than 105 nm, limited by the transmission of LiF windows on cells. The astrophysical implications of our measurements are briefly discussed.

1. Introduction

Despite the much enhanced experimental difficulty of measurements in the vacuum-ultraviolet region at a wave length less than 200 nm, early absorption spectra of gaseous samples provided information, even if largely qualitative, about electronic transitions of simple molecules, analogous to the results of more thorough analysis of spectra practicable in the visible and near-ultraviolet regions. Little information is, however, available about the spectra of these compounds in condensed phases, and even those reported spectra suffer from the challenging experimental conditions of those experiments. A synchrotron is an electron accelerator that provides intense and energetic radiation with a continuous span from the far infrared into the xray region. With such a source of light we have undertaken quantitative measurements of both wave length and intensity for compounds of astrophysical interest, comprising small molecules that exist as gases or vapours at temperature 300 K. To demonstrate the quality of spectra that is achievable with a cryogenic refrigerator coupled to a beam line of the Taiwan Light Source (TLS), we present here spectra of CO, CO_2, NO, N_2O, O_2 and H_3COH in solid phases at 10 K, with other phases for comparison.

These compounds are among the more abundant species of molecular matter discovered through astrophysical observations.

2. Experiments

For these spectral measurements of samples in solid phases at 10 K, we employ a refrigerator system that operates with a Stirling cycle in two stages to attain that temperature.[1-3] As depicted in figure 1, this refrigerator is connected to a beam line of the TLS so that beam of radiation is dispersed with a diffraction grating; by this means we vary the wave length of light incident on a sample that is condensed from the gaseous phase onto a cooled LiF window. Part of the beam before the cryostat is directed to a detector so that we record a ratio of the intensity of light transmitted through the sample to the intensity of the light in the reference beam. From that transmission spectrum of a sample we subtract the spectrum of the background with no sample. This net signal hence becomes available for analysis of the spectral features, which we undertake as follows. For gaseous samples the cryostat is simply replaced with a cell to contain the sample between LiF windows. For our experiments the radiation is limited to a region of wavelength greater than 105 nm by the transmission of LiF windows on our cells.

Our quantitative analysis of spectra of condensed or gaseous samples proceeds as follows. After conversion of wave length to wavenumber, the net absorbance is divided by wavenumber at each point to eliminate the frequency factor in absorption spectra, analysis of the intensity of these spectra shows that the reduced profiles are satisfactorily described with a sum of gaussian contributions, with central wavenumber, width, stature (net absorbance after subtraction of background) and integrated area as fitting parameters. Under these conditions we locate and define both significant electronic transitions and their vibrational substructure, even when the widths of individual contributions are comparable with the differences between adjacent features.

3. Results and discussion

The widths of these electronic and vibrational features evident in the accompanying plots of absorption spectra of the selected molecular samples make difficult their assignment to transitions between particular electronic and vibrational states of molecules in condensed phases, but comparisons with spectra in the gaseous phase, which generally have narrower structure, and with the results of calculations of molecular electronic structure enable at least tentative assignments in most cases. A complicating characteristic of spectra of solid compounds is that the proximity of molecules and the expanded electronic volumes typical of excited electronic states generate strong intermolecular interactions that are absent from gaseous conditions and that calculations on single molecules fail to take into account. For most small molecular species that we have investigated, extensive delocalization in excited electronic states and excitonic phenomena appear to be unimportant despite the broadening phenomenon, but Rydberg transitions seem to be generally absent from spectra of solid samples.[4]

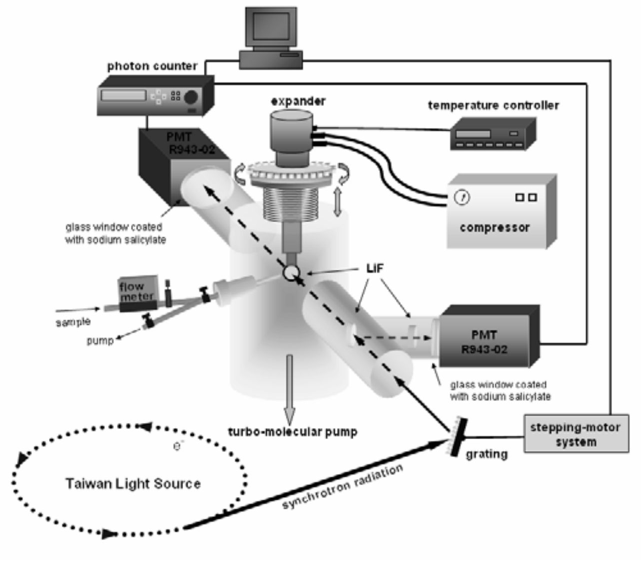

Figure 1. Apparatus employed for measurements of absorption spectra for a sample in a condensed or gaseous phase

As an example of this phenomenon, we show in figure 2 a comparison of spectra of carbon oxide as a gaseous sample, as a pure solid and dispersed in solid argon.[1] Under our conditions of measurements, the absorption spectrum of this gaseous sample in figure 2a shows not only well defined vibrational structure in several progressions that indicate separate upper electronic states but even rotational structure (not visible on the compressed scale of this plot) as either separate rotational lines or incompletely resolved branches. Because rotational motion is strongly inhibited in a pure condensed sample other than dihydrogen H_2 and its isotopic variants, we hereafter ignore this aspect of the spectra. These spectra show that for the first vibrational progression, assigned to an electronic transition A←X, a similar structure is readily discernible under all three conditions of samples, but for only that first electronic transition does the vibrational structure persist in the spectra of our condensed samples. A vestigial second vibrational progression within the region of the first electronic transition is also deduced on fitting the spectra. Relative to the spectrum of pure solid CO in figure 2b, the spectrum of CO dispersed in solid argon in figure 2c at a molar ratio 1:250 exhibits, however, narrower lines for that progression and narrower features ascribed to overlapping electronic transitions at greater wavenumbers.

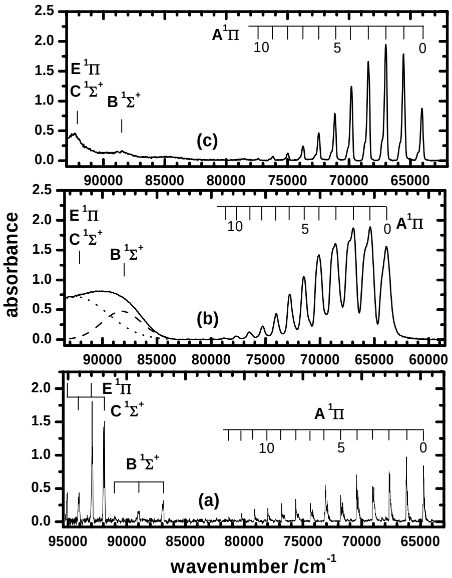

Figure 2. VUV absorption spectra of CO (a) as a gas at 300 K; (b) as a pure solid at 10 K; (c) dispersed in solid Ar (1/250) at 10 K

The differences between the spectra of pure solid CO and of CO dispersed in Ar reflect the extent of isolation of intrinsic molecular properties in the latter condition because the perturbation of a CO molecular species by about twelve atomic Ar entities surrounding it as nearest neighbours is small at energies less than that of the onset of appreciable absorption by solid argon. This isolation that is effective to some extent hence prevents CO molecules from interacting with each other, or, more explicitly, a CO molecule excited to an upper electronic state from interacting with neighbouring CO molecules still in their electronic ground states such that that energy of excitation becomes transferable from one molecular centre to another. An alternative point of view is that a photon is absorbed not at all by one particular molecule, but rather by the collective assembly of molecules; although that point of view might be preferable for the more highly excited electronic states that show a loss of all discernible vibrational structure, the residual vibrational structure in the first electronic transition might warrant the former point of view, namely an absorption event occurring primarily in a particular molecule that is, however, perturbed, and interacting to some extent, with its environment. The energy of excitation arising from an absorption of a photon invariably increases the effective volume of a molecule, because that energy causes an altered distribution of electronic density, corresponding to a decrease thereof near the atomic nuclei and an increase at greater distances from nuclei. For a molecule in a gaseous sample under rarefied conditions such as for figure 1a, such an expansion of electronic density has a negligible effect on other molecules, but in a condensed sample such expansion evidently increases the interaction between neighbouring molecular centres. This effect might increase or decrease the wavenumber of maximum intensity associated with a particular transition, depending on the nature of the interaction. For an absorbing molecule surrounded by other and less polarizable species, an increased wavenumber is commonly observed, but with like molecules a phenomenon akin to resonance might decrease not only the wavenumber of maximum absorption but especially the onset of absorption, so to extend the absorption to the near-ultraviolet region.

The spectrum of pure solid carbon dioxide in figure 3 contains four distinct regions of features − broad and weak lines with maxima near 54300 and 70000 cm^{-1}, a region of resolvable fine structure centred about 79000 cm^{-1} and, beyond 84000 cm^{-1}, a much more intense block of absorption of which the shape is atypical of separate electronic or vibrational transitions; [3] the latter region is satisfactorily fitted with three overlapping lines, consistent with the shape of the curve at the top of the block, with the most intense component extending beyond the range of measurement. The ratio of statures of most intense and least intense fitted components, at either end of the measured spectrum, attains 1000. Between 75800 and 83750 cm^{-1}, as shown in the inset to figure 3, the absorption profile is adequately fitted with 14 lines in a sequence, with mean interval (611±42) cm^{-1} comparable with their fitted widths, of mean (710±190) cm^{-1}. The fact that these widths are comparable with the separations between adjacent members of a vibrational progression in CO_2 obscures this progression to a much greater extent than for the first progression in CO, shown in figure 2b; the separations, unlike the widths, are there much larger, reflecting the attribution of that progression in CO to a stretching vibrational mode but in CO_2 to an angular deformation. For CO_2 even in the gaseous phase, vibrational structure is diffuse at best, unlike the progressions discernible in multiple electronically excited states in the spectrum of CO in figure 2a.

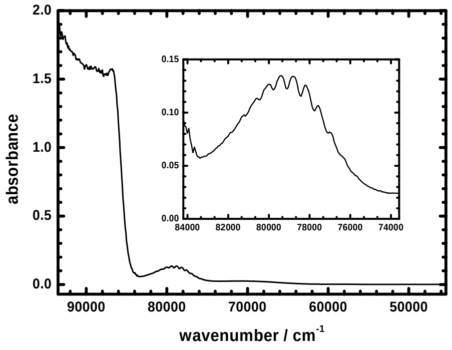

Figure 3. Absorption spectrum of solid CO_2 at 10 K

For pure solid methanol the absorption spectrum [2] in figure 4a is entirely diffuse, exhibiting no individual feature that is separately resolvable or distinct from adjacent features; three components of that total absorption are deducible on fitting with lines of gaussian shape, but those deduced individual properties are by no means unambiguous. In contrast, for methanol dispersed in solid krypton according to the spectrum in figure 4b, the modulation of the absorption profile hints at underlying vibrational structures that are totally obscured in the spectrum of the pure solid. The presence here of vacuum-ultraviolet spectra of CO, CO_2 and H_3COH enables us to make further comparisons related to the size or number of constituent atomic centres of the molecules and the nature of the vibrations. For an isolated or free diatomic molecule, only a vibration described as a bond-stretching mode is possible; for CO the progressions in spectra of either gaseous or condensed samples accordingly show the corresponding intervals of wavenumber. For a free triatomic molecule, both bond-stretching modes and an angular deformation constitute the possible vibrational degrees of freedom; in the spectrum of solid CO_2 in figure 3, only progressions associated with that angular deformation are discernible. For a polyatomic molecule such as methanol with a topology containing four atomic centres H-C-O-H bound in a non-linear sequence, also a torsional vibrational mode is possible;[5] the spectrum of a gaseous sample exhibits much effect of this torsional mode, but its small wavenumber relative to the widths of lines in the solid phase or even for methanol dispersed in solid argon or krypton precludes identification of such vibrational structure with even the most advanced fitting procedures practicable at present.

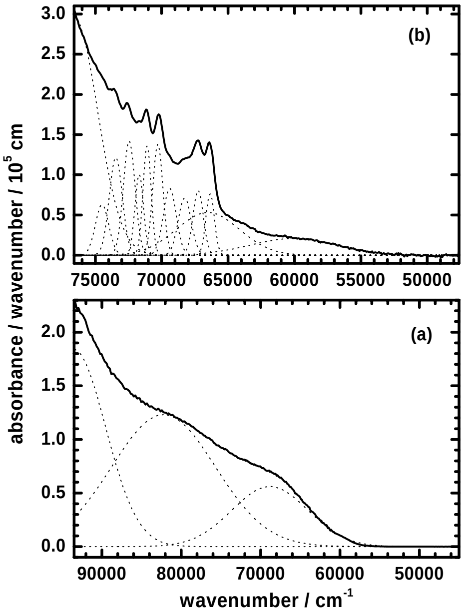

Figure 4. VUV absorption spectra of (a) pure solid H_3COH; (b) $H_3COH/Kr=1/250$, both at 10 K

The spectrum of solid dinitrogen oxide in figure 5 exhibits only four distinct features,[3] but the fit of the total profile near 65000 cm^{-1} and 79000 cm^{-1} seems to require further contributions centred near those locations. The first weak and broad line, with maximum near 55500 cm^{-1}, is practically separate from other features, with the other five overlapping lines on either side of the prominent maximum near 77500 cm^{-1}. Close scrutiny of the residual between the total absorption divided by wavenumber and the sum of those six features indicates the presence of two additional series of weak lines, superimposed on much broader and stronger lines. To fit quantitatively these weak lines in the presence of much more intense and broad features proved impracticable because their statures are at most twice the amplitude of noise, but their widths seem smaller than the separations between adjacent lines. Eight features in the first progression, beginning at 53688 cm^{-1} have a mean separation (1050±71) cm^{-1}

between adjacent features, whereas six features in a second progression, beginning at 64949 cm^{-1}, have a mean separation (674±79) cm^{-1}.

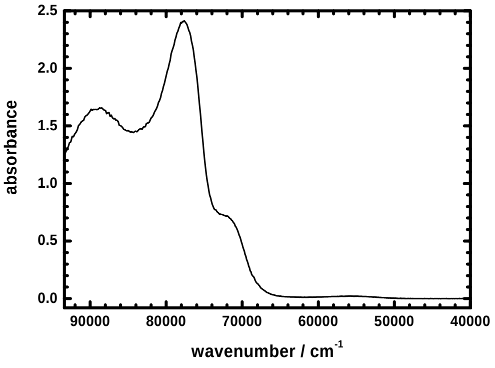

Figure 5. VUV absorption spectrum of pure solid N_2O at 10 K

The spectrum of pure solid dioxygen in figure 6 contains apparently two broad lines, with maxima near 60000 and 72000 cm^{-1},[3] and a hint of a further absorption feature beyond the range of spectral measurement. Fitting the total profile of absorption with three gaussian contributions centred at 56700, 62400 and 72700 cm^{-1}, rather than two, yields a significantly improved fit, but there is otherwise no evident requirement for the middle broad line.

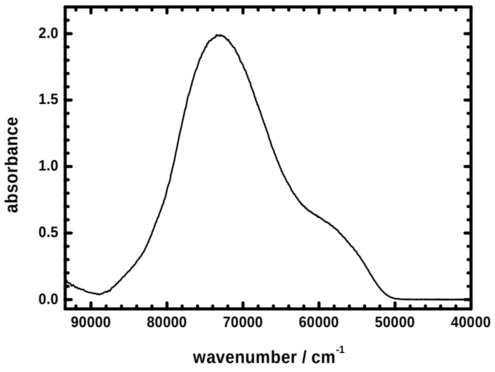

Figure 6. VUV absorption spectrum of pure solid O_2 at 10 K

The curve of pure solid nitrogen oxide in figure 7 contains three readily recognizable features, all broad lines.[3] The most prominent feature occurs before the vacuum ultraviolet region, with a maximum near 48000 cm^{-1}; another feature with maximum near 67000 cm^{-1} is much broader but weaker, and a third continuum extends beyond the limit of measurements as restricted by the LiF windows. Four weak features are barely discernible as a weak modulation of the profile of the subsidiary maximum near 67000 cm^{-1}, with centres near wavenumbers/cm^{-1} 65600, 66800, 68100 and 69300 with uncertainties 200 cm^{-1}, so with an interval approximately 1200 cm^{-1}.

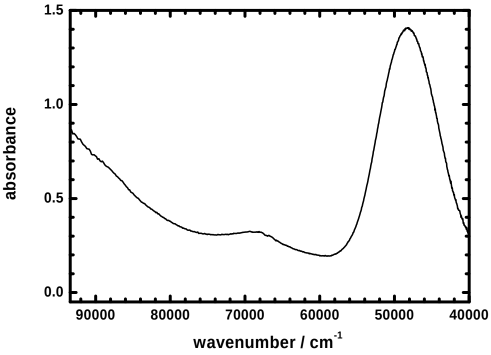

Figure 7. VUV absorption spectrum of pure solid NO at 10 K

The spectrum of solid N_2O in figure 5 hence manifests a significant resemblance to that of solid CO_2 in figure 3, whereas the spectra of solid NO and of solid O_2 in figures 6 and 7 exhibit almost no discernible vibrational structure, in contrast with the spectrum of solid CO in figure 2b. Even for the latter three diatomic species their spectra differ remarkably, but the trend to decreased vibrational structure in these cases bodes poorly for the possibility of discovering vibrational structure in larger molecules containing these moieties.

4. Conclusion

Our survey of spectra in the vacuum-ultraviolet region of selected small molecular species in their pure solid phases, with spectra of gaseous samples or dispersions in solid Ar and Kr for comparison in some cases, indicates a poor prognosis for the prospective identification of these compounds through the measurement of ultraviolet spectra – necessarily in reflectance, because an alternative absorption mode is impracticable –

from the frozen surfaces of astronomical objects such as the farther planets and planetoids. These surfaces would inevitably contain mixtures of compounds, from which broad spectral lines of species such as CO_2, H_3COH, N_2O, O_2, and NO would be distinguishable with only the utmost difficulty. A further complication in the case of such a mixture is that the characteristics of spectral lines of each particular compound would undoubtedly be modified to a greater or lesser extent by the presence of the multiple components of that mixture. For only CO is there a reasonable prospect that its presence might be detected in such an environment by means of vacuum-ultraviolet spectra, even in the presence of its admixture with other compounds. For these discussed molecular species there is little or no absorption in spectra at wave lengths greater than 200 nm, with the prominent exception of NO. In such cases infrared spectra of these surfaces in reflectance might yield more conclusive evidence of the nature of these solid materials. With further data fitted from spectra presented here, we discuss elsewhere [3] also the spectra of solid H_2O (water ice) and solid ammonia, which like most solid compounds discussed above, show only highly diffuse absorption spectra in the vacuum-ultraviolet region.

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