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Solved and unsolved problems of near-threshold spectroscopy of N₂ and CO

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Rotationally resolved jet absorption studies of N₂ at 800–850 Å have led to detailed identifications of the electronic structures associated with low-*J* rovibrational thresholds of ground-state N₂⁺. Of particular interest is a series of perturbed f complexes that interact with core-excited Rydberg levels and, possibly, with the *b'* valence state. The latter assumes the role of a core-excited Rydberg state at high energies and small internuclear distances. A similarly complete picture of the Rydberg structure of CO is still lacking. The interpretation of *ℓ*-uncoupling effects and, thus, the identification of Rydberg complexes is difficult owing to widespread perturbations by non-Rydberg levels. Significant advances have been made in the understanding of the Σ–Σ Rydberg-valence interactions, but few hard facts have emerged concerning the Π–Π interactions where the analysis proceeds in the near-total absence of guidance by theoretical calculations.

1. Introduction

The ability of modern spectroscopic techniques to resolve the rotational structure of molecular transitions at XUV wavelengths shorter than 1000 Å, and the developments in the application of multichannel quantum defect theory (MQDT) to the interpretation of these structures in terms of the rotating and vibrating core and of its interactions with the orbiting Rydberg electron, have led to significant advances in the understanding of rovibronic levels of small molecules at energies approaching the ionization threshold. In addition, state-selective double and triple resonant excitation methods can provide a clear view of Rydberg complexes where, in direct transitions from the ground state, overlapping structures might make it difficult to arrive at unambiguous identifications.

Rydberg states are characterized by vibrational and rotational constants identical to those of the ion core. A full description also requires a set of interaction energies that account for perturbations by valence states; interactions that are expected to scale according to $n^{-3/2}$, where *n* is the principal quantum number of the Rydberg electron. If the core has a low-lying electronically excited state, further complications will arise from interactions with core-excited Rydberg levels. The latter may significantly affect the rotational structure even of high orbital angular momentum states, in marked contrast to Rydberg-valence interactions that are, by and large, restricted to Rydberg levels of low *ℓ* quantum numbers.

From an astrophysical point of view, and in the context of atmospheric studies, a detailed knowledge of perturbations active in the region of strongly absorbing

Rydberg levels is of crucial importance, particularly where the Rydberg-valence interactions open up new decay channels that lead to the photodestruction of the absorbing molecule. For CO it has long been recognized that its photodissociation is dominated by discrete line rather than continuous absorption (Letzelter *et al.* 1987; Van Dishoeck & Black 1988; Viala *et al.* 1988). However, in order to succeed, the modelling of the dissociation process has to depend on a coherent body of reliably derived spectroscopic data including interaction energies. To a significant degree, this goal has been reached by the analysis of the N₂ spectrum, but not yet for the isoelectronic CO molecule where the absence of g/u symmetry amplifies the complexities of the dipole-allowed absorption spectrum and where, so far, very little progress has been made toward a comprehensive description of the Rydberg-valence as well as of the Rydberg–Rydberg interactions.

It is the purpose of this paper to define some of the directions that might be taken by future studies of the electronic structures for the fundamentally important molecules N₂ and CO. The discussion primarily applies to singlet states at energies below the ionization thresholds of N₂ at 125 667.00 cm⁻¹ (Huber & Jungen 1990; Trickl *et al.* 1989) and of CO at 113 027.5 cm⁻¹ (Mellinger *et al.* 1996). Since there are no intracore contributions to spin-orbit interactions between Rydberg levels built on a ²Σ⁺ core, it seems unlikely that significant perturbations will occur between singlet and triplet levels converging to the ground state of the ion. In contrast, such intracore contributions may become important where at least one of the Rydberg levels is built on A ²Π, the spin-orbit coupling constants for the A states of N₂⁺ and CO⁺ being, respectively, -75 and -118 cm⁻¹ (Huber & Herzberg 1979).

The notation used here for Rydberg states is taken from Huber & Jungen (1990). Rydberg states will be written as X⁺(v)nℓλ, A⁺(v)nℓλ, ... or X⁺nℓλ, A⁺nℓλ, ..., where the X ²Σ⁺ or A ²Π core configurations of the ion precede, in abbreviated form and with or without vibration, the semiunited atom description (Mulliken 1967, 1976) of the Rydberg orbital. Further definition by the resulting A and multiplicity will, in general, not be necessary since the discussion is mostly limited to spin- and dipole-allowed transitions from the X ¹Σ⁺ ground state.

2. Experimental details

The absorption spectra of pure nitrogen jets and of supersonic expansions of N₂ or CO mixed with He have been photographed with a resolution of 0.5 cm⁻¹ using the 6.65 m spectrograph at the Photon Factory synchrotron facility of the National Laboratory for High Energy Physics in Tsukuba (Japan), and with a somewhat lower resolution of *ca.* 1 cm⁻¹ at the 10.6 m vacuum ultraviolet (VUV) spectrograph of the Observatoire de Paris–Meudon where the background continuum is emitted from a vacuum spark that operates in synchronization with a pulsed nozzle. The small gas throughput of the pulsed jet makes it economical to use for the study of rotationally cold spectra of rare isotopic species or of highly toxic or corrosive gases. In the present work it has been used to record the spectra of the four main isotopes of CO (12–16, 12–18, 13–16 and 13–18). Details of the experiments may be found in earlier publications (Huber *et al.* 1993, 1994; Rostas *et al.* 1994).

The very limited dynamic range of photographic plates provides a strong argument against the continued use of large scale spectrographs working in photographic mode, and the same can be said of the rather lengthy and cumbersome measuring routines that are used for the interpolation and calibration of the wavelengths

of the recorded spectral lines. On the positive side, however, one must point out the multiplex advantage of the photographic technique—not yet offered by Fourier transform spectrometers working in the extreme ultraviolet region—that allows for the recording of a wavelength interval of more than 200 Å in a single exposure and with a resolution that is sufficient for unambiguous assignments to be made in many instances. To record the same interval at the higher resolution of a tunable laser experiment would be very time consuming. Also, in the case of a multiphoton ionization experiment, some information readily obtained from the absorption spectrum will be missed where the transfer of level populations into the ionization continuum has to compete with other non-radiative decay processes (Eikema *et al.* 1994a).

3. The near-threshold absorption of N_2

The N_2 absorption at wavelengths from *ca.* 850 Å to the ionization limit near 796 Å is characterized by the gradual transition with increasing energy from a spectrum composed of vibrational progressions associated with several electronic states to a spectrum of electronic progressions converging to the lowest vibrational thresholds in the $\dots 2\sigma_u^2 1\pi_u^4 3\sigma_g$, $X^2\Sigma_g^+$ ground state of N_2^+ . The series of p complexes can be followed to $n = 39$, and the highest member identified in the much weaker series of f complexes has $n = 15$ (Chang & Yoshino 1983; Huber & Jungen 1990). Dominating the entire region are two strong progressions in the vibrational frequency of the $\dots 2\sigma_u^2 1\pi_u^3 3\sigma_g^2$, $A^2\Pi_u$ first excited state of N_2^+ . The stronger progression, with red-shaded bands near 122 155 and 123 990 cm^{-1} and a very broad diffuse region at around 125 830 cm^{-1} , belongs to the $\dots 2\sigma_u^2 1\pi_u^3 3\sigma_g^2 3d\delta$ or $A^+3d\delta$, core-excited $^1\Pi_u$ Rydberg state (see figure 1 of Huber *et al.* (1994) and references therein). The $v = 3$ level is involved in a complex resonance located just below the $X^2\Sigma_g^+$ ($v = 1$), or $X^+(1)$, threshold near 127 630 cm^{-1} (McCormack *et al.* 1992).

The second progression begins at 121 121 cm^{-1} with a red-shaded band which, following Kosman & Wallace (1985), has been assigned to the $A^+(0)3d\sigma$ state (Huber & Jungen 1990). Higher members in the progression at around 122 980 and 124 860 cm^{-1} are more difficult to recognize owing to the leakage of intensity to neighbouring transitions which produces the complex sprawling structures that are in striking contrast with the comparatively narrow band contours of transitions to $A^+(0)3d\delta$ and $A^+(1)3d\delta$. The autoionizing fourth member of the progression, $A^+(3)3d\sigma$, has been identified near 126 685 cm^{-1} in an interaction with the $X^+(1)10f$ complex (McCormack *et al.* 1991).

A reproduction of the spectrum near 121 100 cm^{-1} can be seen in figures 5 and 6 of Huber *et al.* (1994). The analysis shows the $A^+(0)3d\sigma$ core-excited level to interact with the $X^+(0)5f$ and $X^+(1)4f$ complexes located at higher and lower energies, respectively. The repulsion by the central $^1\Pi_u$ perturber separates the Π from the Σ , Δ and Φ components of the f complexes, pushing them to the top or bottom of the perturbed A structures. The interpretation of the observed bands was confirmed with the help of MQDT calculations which reduce the three-state interaction to a set of diagonal and off-diagonal quantum defects and their energy dependences. The results reproduce the observed transitions with a standard deviation of 0.40 cm^{-1} .

The $A^+(1)3d\sigma$ level at 122 987 cm^{-1} is involved in a very similar interaction with $X^+(2)4f$, the latter appearing in the spectrum with an intensity that vastly exceeds expectations based on Franck–Condon factors for ionizing transitions to the lowest vibrational levels of ground-state N_2^+ . The spectrum is reproduced in figure 1. The

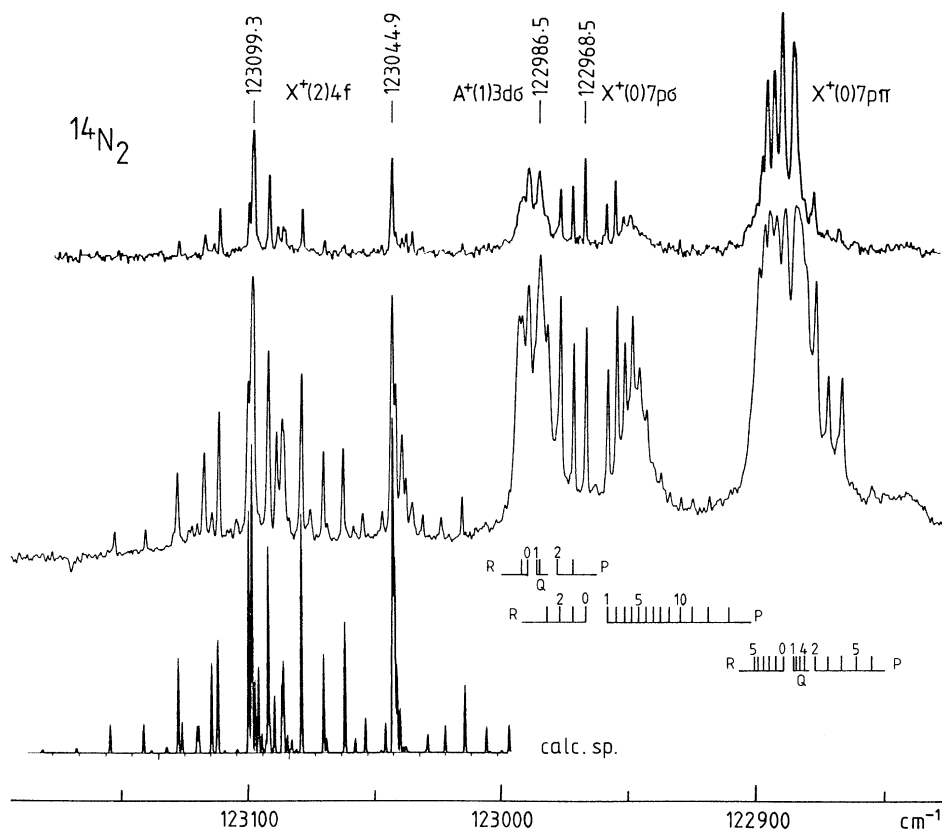


Figure 1. Jet absorption spectra of N_2 at two different reservoir pressures, 811.7 and 814.1 Å (Tsukuba, 6.65 m spectrograph). The $X^+(2)4f$ complex is compared with a calculated spectrum.

interaction is further complicated by the presence of the $X^+(0)7p$ complex where the Π component has long been known to be displaced by -24 cm^{-1} from its predicted position (Huber & Jungen 1990). Again, the core-excited level pushes the Π component of the f complex by *ca.* 50 cm^{-1} to the top of the A structure, leaving a prominent Σ component at $123\,045 \text{ cm}^{-1}$ well separated from the rest of the f complex and exposed to homogeneous perturbations of the higher- J levels by $X^+(0)7p\sigma$. As shown in figure 1, the MQDT least-squares calculations reproduce the observed transitions to $X^+(2)4f$ quite well, leaving only minor discrepancies unaccounted for on the high-energy side of the f complex and failing to reproduce fully the width of the only partly resolved Σ component at $123\,045 \text{ cm}^{-1}$.

Unexpected is the lack of evidence for the occurrence of a heterogeneous perturbation of $X^+(0)7p\sigma$ by $A^+(1)3d\sigma$. This interaction results from the combined effects of ℓ uncoupling and a homogeneous perturbation and it produces in the calculations, but apparently not in the spectrum, a clearly avoided crossing near $J = 4$. The absence of this perturbation is particularly evident from the perfectly regular behaviour of the P branch in the $X^+(0)7p\sigma$ band at around $J' = 4$. It suggests that the rotational interaction of $X^+(0)7p\sigma$ with the $7p\pi$ component mixed homogeneously into $A^+(1)3d\sigma$ interferes destructively with a second matrix element—not yet fully accounted for by the calculations—that represents the rotational interaction of $A^+(1)3d\sigma$ with a suitably chosen $^1\Sigma_u^+$ configuration mixed into $X^+(0)7p\sigma$.

An attractive choice is $b' {}^1\Sigma_u^+$. This valence state is partly described by the configuration $\dots 2\sigma_u^2 1\pi_u^3 3\sigma_g^2 1\pi_g$, which closely resembles the configuration of a core-excited Rydberg state, particularly at short internuclear distances where the antibonding $1\pi_g$ orbital is subject to Rydbergization (Mulliken 1976, 1977), assuming the characteristics of a $3d\pi$ Rydberg orbital, and thus establishing a 'pure precession' relation with $A^+3d\sigma$.

The f series of absorption bands is remarkable both for its weakness and for the unpredictability of its band structures. The $X^+(0)4f$ complex appears very weakly at $118\,730\text{ cm}^{-1}$ of the absorption spectrum (Huber *et al.* 1994). Apart from minor local interactions with two overlapping levels, one of them $b'(23)$, it presents an almost unperturbed picture with a Λ structure that can be predicted from a knowledge of the quadruple moment and anisotropic polarizability of the N_2^+ core. Unusual, however, is the absence of all Q branch transitions to f parity levels of the complex, while e parity levels are seen in P as well as R branch transitions. This appears to be a purely parallel band that borrows its intensity from an unidentified ${}^1\Sigma_u^+ \leftarrow X {}^1\Sigma_g^+$ transition.

Q branches are similarly weak in the rather isolated $X^+(0)6f \leftarrow X(0)$ band at $122\,600\text{ cm}^{-1}$ (see figure 2*b* of Huber & Jungen (1990) and figure 7 of Huber *et al.* (1994)), but they tend to be much stronger in transitions to f complexes that happen to be close to core-excited $A^+3d\sigma$, ${}^1\Pi_u$ levels where they benefit from the large transition dipole amplitudes to the latter. This erratic behaviour, taken together with the general weakness of the bands, seems to indicate that the f series of absorption bands has no intensity of its own and that the bands appear solely on account of channel interactions with much stronger perpendicular and/or parallel transitions.

The absence of intrinsic oscillator strength for the X^+nf absorption series can be anticipated from a simple consideration of the $3\sigma_g$ core and $nf\lambda$ Rydberg orbitals involved in the transitions. Mulliken (1967, 1976) considers the $3\sigma_g$ core orbital to be of $3d\sigma$ type, though greatly reduced in size compared to a $3d$ orbital of a typical first-row atom. Johns (1974), on the other hand, attributes mostly s, rather than d, character to the same orbital on the basis of a comparison of observed with calculated rotational branch intensities in transitions to p complexes. In either case, spatial overlap of $3\sigma_g$ with the non-penetrating and much larger f orbitals will be negligible and will make no significant contribution to the radial electronic dipole integrals $a^{(\lambda)}$ in equation (7) of Huber *et al.* (1994). From an s-type $3\sigma_g$ orbital, access to the f Rydberg orbitals is further restricted by the $\Delta\ell = \pm 1$ orbital angular momentum selection rule.

The $b' {}^1\Sigma_u^+$ state is known to be strongly perturbed all the way up to its highest observed level $v = 43$ at $126\,385\text{ cm}^{-1}$ (Huber & Jungen 1990; McCormack *et al.* 1990), but the true origin of the perturbations in the near-threshold region has never been examined and is usually blamed, by extrapolation, on the same interactions with p complexes that have been scrutinized at lower energies (Stahel *et al.* 1983). To the extent that for high energies and short internuclear distances the $b' {}^1\Sigma_u^+$ state represents the $n = 3$ lowest member of the $A^+nd\pi$ Rydberg series, transitions to its high vibrational levels will be intensified by a 'discrete' shape resonance in the $nd\pi_g \leftarrow 1\pi_u$ excitation channel (Kosman & Wallace 1985). It remains to be seen if some of this enhanced oscillator strength finds its way into transitions to f complexes through homogeneous b' state interactions of $A^+3d\pi$ with $X^+nf\sigma$ that parallel the now well-established $A^+3d\sigma$ - $X^+nf\pi$ perturbations discussed previously.

4. The CO absorption spectrum at $\lambda < 1000 \text{ \AA}$

Komatsu *et al.* (1995) have summarized the results of a series of triple-resonant multiphoton ionization and ion dip experiments that have unambiguously identified eight Rydberg series of singlet s, p, d and f complexes converging to $v = 0$ and 1 of the $X^2\Sigma^+$ ground state of CO^+ . For the most part, they confirm and complement earlier assignments made in the one-photon absorption spectrum of CO (Ogawa & Ogawa 1972, 1974; Casey 1978; Eidelsberg & Rostas 1990; Eidelsberg *et al.* 1992). The series of core penetrating low orbital angular momentum states are widely perturbed, with the exception of $X^+np\sigma$, where for low-to-medium n values the quantum defects are found to display a rather smooth and linear dependence on energy (Rostas *et al.* 1994; Komatsu *et al.* 1995). Data for the d complexes are still incomplete and none of the f complexes detected by triple resonant excitation via the $3s\sigma$ or $3p\sigma$ Rydberg levels have been identified in the one-photon absorption spectrum. As for N_2 , the weakness of transitions from the $X^1\Sigma^+$ ground state of CO to the X^+nf Rydberg levels is very probably the consequence of negligible spatial overlap of the compact core orbitals with the non-penetrating and diffuse $nf\lambda$ Rydberg orbitals.

Triplet levels arising from the same Rydberg configurations have recently been studied by laser-reduced fluorescence spectroscopy using state specific two- and three-step excitation techniques (Mellinger 1995; Mellinger & Vidal 1994, 1995; Mellinger *et al.* 1996). An MQDT treatment of p and d levels at energies from *ca.* 105 000–112 000 cm^{-1} has estimated the first ionization potential of CO at the value quoted in § 1. Allowing for interactions between series of different ℓ , the calculations predict the positions of the still missing $ns\sigma$, $np\pi$ and $nd\pi$ triplet series and they explain the absence of the $ns\sigma$ series by its nearly complete mixing with the $nd\sigma$ states. The details for a series of X^+nf triplet complexes have yet to be published; most puzzling is the observation (Mellinger 1995) that the f triplet levels lie above, rather than below, the corresponding singlet complexes with level widths that are much broader for the former than for the latter.

So far, the investigation of the singlet series converging to $X^2\Sigma^+$ has failed to provide clear-cut evidence of mixing between states of different orbital angular momentum ℓ , although Ebata *et al.* (1992) and Komatsu *et al.* (1993, 1994) have pointed out that the effective ℓ values derived from ℓ uncoupling effects in p complexes amount to only *ca.* 80% of expectations for a pure p complex. However, similar reductions might also result from the contamination of Rydberg by non-Rydberg configurations; *ab initio* calculations by Cooper & Kirby (1987, 1988) and Kirby & Cooper (1989) have, indeed, predicted the lowest Rydberg levels of $^1\Sigma^+$ and $^1\Pi$ symmetries to be strongly mixed with valence state configurations. The following discussion explores several regions of the absorption spectrum that are significantly shaped by homogeneous Rydberg–non-Rydberg interactions, either between Σ levels involving the well-established D' valence state (Wolk & Rich 1983), or between Π levels involving at least one valence state which still has to be fully characterized. Details of the analyses will be published elsewhere.

Perturbations of the singlet $X^+(v)ns\sigma$ levels result from strong interactions with the repulsive part of the $D'^1\Sigma^+$ potential curve. The effects of the Rydberg–valence interaction on vibronic energies and level widths in the $X^+3s\sigma$ state ($B^1\Sigma^+$) have been investigated by Tchang-Brillet *et al.* (1992), who estimated the interaction matrix element at *ca.* 2900 cm^{-1} . Line shifts and predissociation widths increase from $v = 0$ –2, and the $v = 3$ level of $^{12}\text{C}^{16}\text{O}$, just below the potential hump of the

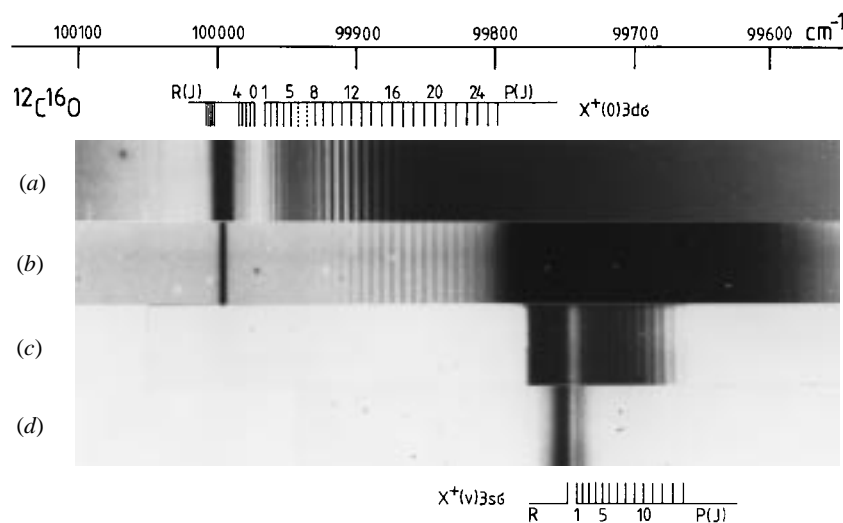


Figure 2. (a)–(c) Room temperature absorption spectra of $^{12}\text{C}^{16}\text{O}$ for three different column densities; (d) jet absorption spectrum, $\lambda = 999.0\text{--}1004.5 \text{ \AA}$ (Meudon, 10.6 m spectrograph).

double-minimum state created by the avoided crossing, is found to be completely diffuse (Baker *et al.* 1995).

We have identified an additional vibrational level of $X^+3s\sigma$ near $99\,800 \text{ cm}^{-1}$ (Eidelsberg *et al.* 1996, unpublished results). The new level lies clearly above the avoided crossing of $X^+3s\sigma$ with the D' valence state, having $v = 6$ or 7 , and it is involved in a homogeneous interaction with the nearly coinciding $X^+(0)3d\sigma$ state. The spectrum of $^{12}\text{C}^{16}\text{O}$ is reproduced in figures 2a–c for three different column densities at room temperature and it is compared in figure 2d with the rotationally cold spectrum of a jet expansion. The deperturbed $3s\sigma$ and $3d\sigma$ levels cross near $J = 7$ or 8 and, based on the nearly complete transfer of intensity at these J values from the higher to the lower interaction partner, we conclude that the unperturbed transitions are of about equal intensities. In $^{12}\text{C}^{18}\text{O}$ (figure 3) and $^{13}\text{C}^{16}\text{O}$, the deperturbed $3s\sigma$ levels have dropped entirely below $3d\sigma$ and have become narrower. In contrast, the higher lying $3d\sigma$ levels are now totally diffuse, giving rise to broad, structureless R and P branches which are separated by an ill-defined zero gap near $99\,900 \text{ cm}^{-1}$.

Similarly, a strong $\Sigma\text{--}\Sigma$ transition of $^{12}\text{C}^{16}\text{O}$ near $109\,450 \text{ cm}^{-1}$ has tentatively been assigned to the $X^+(4)4s\sigma$ level just above the avoided crossing of $X^+4s\sigma$ with $D'^1\Sigma^+$ (Rostas *et al.* 1994). The analysis of the complex structure, shown in figure 4, reveals a homogeneous interaction of $X^+(4)4s\sigma$ with the σ component of the $X^+(3)4p$ complex. In terms of pure Rydberg configurations, this $\Delta v = 1$ interaction is Franck–Condon forbidden, just like the interaction described above between the $v = 0$ and $v = 6$ or 7 levels of the $3d\sigma$ and $3s\sigma$ states built on $X^2\Sigma^+$. Both interactions are made possible by the mixing primarily of $X^+3s\sigma$ and $X^+4s\sigma$ with the repulsive part of $D'^1\Sigma^+$, where the vibrationally excited $X^+ns\sigma$ levels also benefit from the large $D' \leftarrow X$ transition moment (Kirby & Cooper 1989). In both instances, the mixing with $D'^1\Sigma^+$ leads to strongly isotope-dependent predissociation. In figure 4, isotope shifts of the order of 140 cm^{-1} are seen to transform the comparatively sharp bands at around $109\,460 \text{ cm}^{-1}$ of the main isotope into three completely diffuse, structureless peaks of $^{13}\text{C}^{16}\text{O}$ near $109\,320 \text{ cm}^{-1}$.

The identification of the new Σ levels above the avoided crossings of D' with the

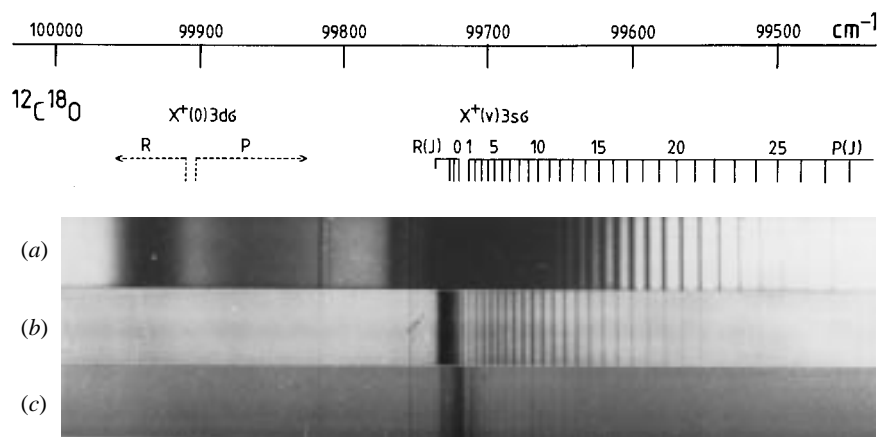


Figure 3. (a)–(b) Room temperature absorption spectra of $^{12}\text{C}^{18}\text{O}$ for two different comolumn densities; (c) jet absorption spectrum, $\lambda = 1000.0\text{--}1005.5 \text{ \AA}$ (Meudon, 10.6 m spectrograph).

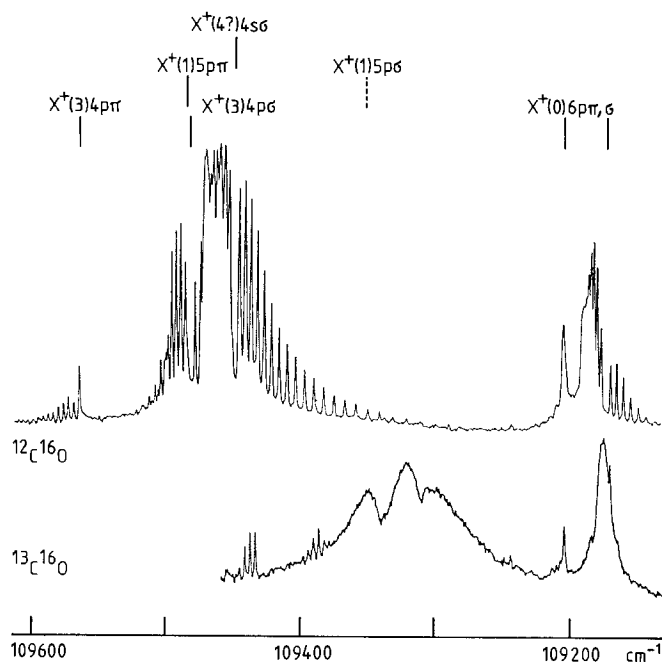


Figure 4. Jet absorption spectra of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$, $\lambda = 912.4\text{--}916.3 \text{ \AA}$ (Meudon, 10.6 m spectrograph). Band identifications at the top of the figure refer to the main isotope.

$n = 3$ and 4 members of the $X^+ns\sigma$ series provides valuable information that will help tie down the exact shape of the repulsive branch of the D' state potential curve, paving the way to more reliable predictions of the predissociation widths.

The only theoretical predictions on Π Rydberg levels and their interactions with valence states come from the *ab initio* calculations of Cooper & Kirby (1988). However, these calculations stop at the third root of $^1\Pi$ symmetry, and although it becomes clear that the Rydberg levels built on the $X^2\Sigma^+$ core will strongly mix with the core-excited $A^+3s\sigma$ configuration as well as with valence configurations, it

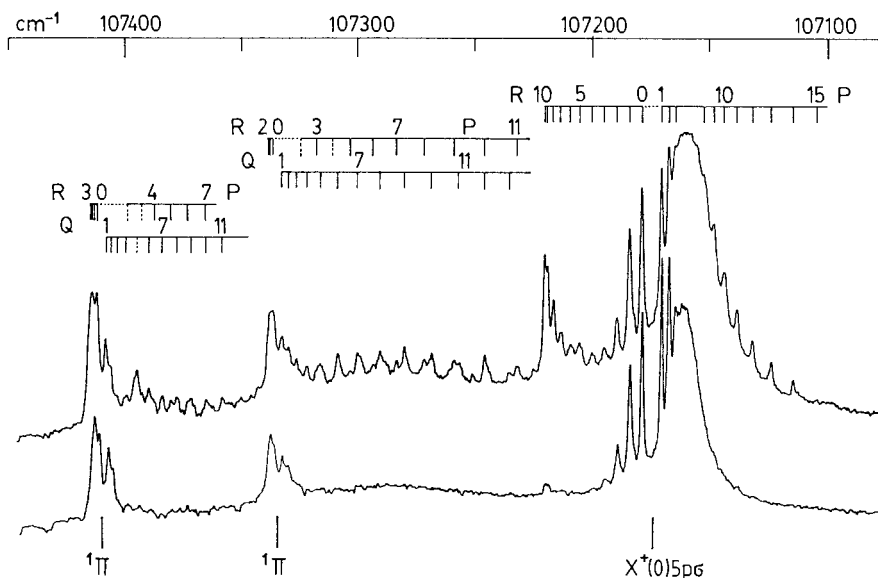


Figure 5. Jet absorption spectra of $^{12}\text{C}^{16}\text{O}$ at two different reservoir pressures in the 930.7–933.7 Å region of the $X^+(0)5p$ complex (Tsukuba, 6.65 m spectrograph).

is not yet readily possible to picture the course of the diabatic potential curves that are frequently helpful as a guide to the analyses of perturbed spectra.

The absorption spectrum provides numerous examples of $^1\Pi$ levels which fit neither the description of a Rydberg state built on $X^2\Sigma^+$ nor that of a core-excited state. In figure 3 of Rostas *et al.* (1994), one such unidentified non-Rydberg level can be followed as it shifts, upon isotopic substitution, through the region of the $X^+(0)4p$ complex, gradually losing the $^1\Pi \leftarrow X^1\Sigma^+$ transition dipole moment picked up from $X^+(0)4p\pi$ of $^{12}\text{C}^{16}\text{O}$, and finally disappearing inside the $X^+(0)4p\sigma$ component of $^{13}\text{C}^{18}\text{O}$ where it can be traced by the effects of its J -dependent interaction with the Σ state. The fit of the data for $^{13}\text{C}^{18}\text{O}$ to the eigenvalues of a Hamiltonian matrix that includes the $X^+(0)4p$ complex together with two homogeneously interacting $^1\Pi$ perturbers, but excludes any direct interactions of the latter with the Σ state of the complex, reproduces the observations with a standard deviation of 0.12 cm^{-1} . This is nearly as good as the fit carried out by Eikema *et al.* (1994b) who treated the perturbation of the $^1\Sigma^+$ Rydberg by the overlapping $^1\Pi$ non-Rydberg level as a direct two-state heterogeneous interaction, ignoring the fact that such an interaction would be configurationally forbidden. Similar fits for the other three isotopes are less satisfactory, leaving the impression that not all interactions have been accounted for.

A very different situation occurs in the region of the $X^+(0)5p$ complex (figure 5). The $5p\sigma$ component is readily recognized in its predicted place at 107174 cm^{-1} , partly overlapped by the high-energy wing of a strong and diffuse absorption feature at 107160 cm^{-1} . Less obvious is the identification of $X^+(0)5p\pi$. The clue comes from the rotational structure of the $5p\sigma$ component which probes, through ℓ uncoupling interactions, the $5p\pi$ content of surrounding $^1\Pi$ levels. It turns out that for low rotation, $5p\pi$ is represented by the diffuse band at 107160 cm^{-1} , having dropped below $5p\sigma$ as the result of interactions with two weakly bound non-Rydberg $^1\Pi$ levels which give rise to strongly red-shaded bands at 107336 and 107412 cm^{-1} , and which assume the role of $5p\pi$ for high rotation. Accordingly, the $P(1)$ line of the Σ^-

Σ band, associated with the only $X^+(0)5p\sigma$ rotational level that does not mix with $^1\Pi$, is found to be sharp, both in the absorption spectrum and in the $1XUV + 1UV$ photoionization spectrum of Eikema *et al.* (1994a). As J increases, the line widths broaden and the photoionization signal disappears, and at about $J = 5$, the R branch in the absorption spectrum begins to turn around and forms a head at $107\,220\text{ cm}^{-1}$, indicating that the $5p\pi$ interaction partner is now to be found at energies above, rather than below, the $5p\sigma$ levels.

From the *ab initio* calculated potential energy curves of Cooper & Kirby (1988), it is clear that the internuclear distances predicted for the $^1\Pi$ valence configurations are too large for these states to be observed from $v = 0$ of $X^1\Sigma^+$, except where the non-Rydberg levels reach into the Franck–Condon allowed region through interactions with Rydberg levels built on $X^2\Sigma^+$ or $A^2\Pi$. The relevant matrix elements which accomplish the transfer of absorption oscillator strength from the $X^+(0)4p\pi$ and $5p\pi$ levels to various non-Rydberg perturbers are of the order of $10^1\text{--}10^2\text{ cm}^{-1}$, and similar interactions may possibly account for the appearance of additional unidentified $^1\Pi$ levels at higher energies. Frequently, however, the interactions are much less conspicuous and lead to nothing more than small local perturbations that are limited to a narrow range of J values. One such example has emerged from the analysis of the $^{12}\text{C}^{16}\text{O}$ spectrum in figure 4 where—in addition to the strong interaction of $X^+(4)4s\sigma$ with $X^+(3)4p\sigma$ —the least-squares fits have revealed the existence of a dark $^1\Pi$ perturber which affects both the low- J region of $X^+(1)5p\pi$ and the high- J levels of $X^+(4)4s\sigma$. The perturbation in $X^+(1)5p\pi$ was not noticed in the triple-resonant ion-dip spectra of Komatsu *et al.* (1993), but its effect is clearly seen in the absorption spectrum. Inclusion of the dark perturber state in the Hamiltonian matrix leads to a striking improvement of the least-squares fits which reproduce the entire spectrum from $109\,300\text{--}109\,600\text{ cm}^{-1}$ with a standard deviation of better than 0.20 cm^{-1} . The heterogeneous interaction with $X^+(4)4s\sigma$ confirms the latter to be of mixed, rather than pure s, character with an orbital angular momentum that can be uncoupled by rotation.

5. Conclusions

The near-threshold absorption of N_2 is characterized by the interactions of core-excited 3d levels, particularly of $A^+3d\sigma$, with the p and f series of Rydberg levels converging to the ground state of N_2^+ . The analysis has progressed to the point where it becomes feasible to attempt a global fit of the observed band structures using MQDT least-squares computational methods. Future work will focus on the long-neglected $b^1\Sigma_u^+$ valence state which turns into a core-excited 3d state at short internuclear distances, possibly playing a significant role as the $A^+3d\pi$ perturber of the erratically behaving Rydberg series of f complexes.

For the isoelectronic CO molecule, progress in the description of the $X^+ns\sigma$ series of Rydberg levels comes from the extension of the analyses for the first two members into the regions above the avoided crossings of $n = 3$ and $n = 4$ with the repulsive wall of the $D^1\Sigma^+$ valence state. In addition, homogeneous interactions of the π components of $X^+(0)4p$, $X^+(0)5p$ and $X^+(1)5p$ with $^1\Pi$ levels of much smaller B values have been studied. So far, no coherent picture has emerged for the valence state believed to be the instigator of the perturbations.

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de Paris–Meudon have been recorded by F. Launay, and M. Eidelsberg has contributed to the analyses and data reduction for four CO isotopomers. The interpretation of the N_2 spectrum would not have progressed as far as it did without the expert handling of the MQDT calculations by Ch. Jungen of the Laboratoire Aimé Cotton in Orsay. It is a pleasure to acknowledge the hospitality enjoyed during repeated visits to the host institutions in Japan and France. Finally, I thank R. W. Field for his helpful comments regarding this work, as well as J. K. G. Watson for his critical reading of the manuscript.

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