Molecular photoionization as a probe of vibrational–rotational–electronic correlations
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Molecular photoionization as a probe of vibrational–rotational–electronic correlations

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We determine the rotationally state-resolved \(2\sigma_u^{-1}\) photoionization of \(\text{N}_2\) into alternative vibrational channels as a function of energy over a 200 eV range. Experiment and theory reveal that Cooper minima highlight the coupling between electronic, vibrational, and rotational degrees of freedom over this very wide range. © 1996 American Institute of Physics. [S0021-9606(96)03023-1]

Studies of photoion vibrational and rotational distributions provide valuable insights into microscopic aspects of molecular photoionization dynamics.1–13 Vibrationally resolved spectra probe correlations between photoelectron motion and molecular geometry,1–4 while rotationally resolved data elucidate the coupling of angular momenta between the continuum electron and the ion core.5–10,12,13 Our group has recently performed both types of measurements over an extremely broad range,11–13 emphasizing that molecular aspects of the photoejection process extend far (i.e., > 200 eV) into the ionization continuum. These vibrationally resolved studies of \(\text{N}_2\) \(2\sigma_u^{-1}\) photoionization showed that Cooper minima can lead to non-Franck–Condon behavior over a broad energy range.11 We have also studied the evolution of the \(\text{N}_2^+(B^2 \Sigma_u^+, v^+=0)\) rotational distributions with photoelectron energy, and identified the strong influence of Cooper minima on angular momentum partitioning between the photoelectron and the photoion.12,13 In this Communication, we report the first study which combines these previous two types of investigations — specifically, by resolving ionic ro-vibrational states over a wide energy range. We present both experimental and theoretical results on \(\text{N}_2^+(B^2 \Sigma_u^+)\) rotational distributions for \(v^+=0\) and \(v^+=1\) following \(\text{N}_2\) \(2\sigma_u^{-1}\) photoionization in the region \(25 \leq h\nu_{\text{exc}} \leq 210\) eV. By contrasting the rotational distributions for alternative photoion vibrational levels, we investigate fundamental aspects of the dynamics of coupling between electronic and nuclear motion. By simultaneously determining the vibrational and rotational energy deposition into the photoion, this study is the first investigation of its type into vibrational–rotational–electronic (V–R–E) coupling over a broad range of electron energy.

The previous \(\text{N}_2\) \(2\sigma_u^{-1}\) studies11–13 and the present investigation cover a range which includes two Cooper minima, and the dominant effects that we observe result from these minima. The present study provides further progress in understanding general aspects of molecular Cooper minima, which are not as fully characterized as those for atomic systems.14 A Cooper minimum occurs when a principal-value partial wave component of the photoionization matrix element changes sign.14 This results in a minimum or an inflection point in the cross-section, and an oscillation in the photoelectron asymmetry factor \((\beta)\). Molecular Cooper minima have been investigated previously.11–13,15–17 The minimum must occur in a dominant channel if it is to have an appreciable effect on the integrated cross section. While the effects of Cooper minima on photoelectron angular distributions have been studied in detail,14 their significance for ion vibrational and rotational motions is only beginning to be unraveled. This is because such studies of Cooper minima frequently require broad spectral coverage,19 which is difficult to achieve with photoelectron spectroscopy. While both REMPI/PES8,9,16,17 and ZEKE/PFI5,7,18 studies have generated rotationally resolved photoelectron results, these methods are limited to near-threshold or threshold studies, respectively.

Our experimental technique of detecting dispersed fluorescence from excited photoions12 circumvents resolving power limitations of photoelectron spectroscopy. When the photoion is created in an excited state, it can either fragment20 or fluoresce.21 By dispersing the fluorescence, the detection bandwidth in such an experiment is decoupled from the excitation bandwidth. This enables us to obtain highly resolved data on the photoions while exploiting the broad tunability of synchrotron radiation. Our previous experiments employing dispersed fluorescence to compare the photoion rotational distributions for \(\text{N}_2\) and CO demonstrated that the \(\text{N}_2\) \(2\sigma_u^{-1}\) distributions begin changing rapidly above \(h\nu_{\text{exc}} \approx 100\) eV due to the presence of pronounced Cooper minima in the \(l=2\) and 4 partial waves of the \(2\sigma_u^{-1} \rightarrow k\sigma_g^{-1}\) channel. In more recent measurements of \(\text{N}_2\) \(2\sigma_u^{-1}\) photoion vibrational distributions, we have shown that the \(R\)-dependence of the Cooper minima results in the breakdown of the Franck–Condon approximation over the broadest energy range observed to date.11 In this Communication, our experiments and calculations show that the same
Briefly, nitrogen molecules are photoionized, and the fluorescence from the excited photoions is collected, dispersed, and detected. The excitation-fluorescence sequence is the same as that used previously, only this time we detect rotationally resolved fluorescence from both \( v^+ = 0 \) and \( v^+ = 1 \) simultaneously.

\[
\text{N}_2(X^1Σ^+_g, v_0=0, (N_0)) + hν_{\text{exc}} \rightarrow \text{N}_2^+(B^2Σ^+_u, v^+, N^+) + e^- \\
\downarrow \\
\text{N}_2^+(X^1Σ^+_g, v^+, N^+) + hν_{\text{exc}}, e^{-}. (1)
\]

The \( \text{N}_2 \) gas is introduced into the interaction region via a free-jet supersonic expansion to limit the number of target rotational states. We estimate the rotational temperature of the \( \text{N}_2 \) target molecules to be 20 K, using comparisons with the same as that used previously, only this time we detect rotationally resolved fluorescence from both \( v^+ = 0 \) and \( v^+ = 1 \) simultaneously. The excitation-fluorescence sequence is the same as that used previously, only this time we detect rotationally resolved fluorescence from both \( v^+ = 0 \) and \( v^+ = 1 \) simultaneously.

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quently enhanced at higher energies, large $\Delta N$ transitions start to dominate earlier in the photoionization to $v^+ = 1$. As a result, the \text{"fork\"} observed for the relative rotational populations seen in Fig. 3 at $h\nu_{\text{exc}} \approx 120$ eV tracks the divergence of the vibrationally resolved Cooper minimum shift seen in the bottom frame of Fig. 4. The $k\sigma_u$, $l = 4$ component also displays a Cooper minimum. Its behavior is similar to that of $l = 2$, and will be discussed in detail elsewhere.\(^3\)

There are two likely causes for the shifting of these Cooper minima,\(^1\)\(^2\)\(^3\) which can be distinguished as initial and final state effects. The initial state contribution arises from the variation of the angular momentum composition of the target $2\sigma_u$ orbital with internuclear distance. Because photoionization to alternative photoion vibrational levels has the effect of emphasizing different regions of $R$, the extent to which a Cooper minimum contributes to the cross section will vary with photoion vibrational level. However, the $2\sigma_u$ orbital composition evolves only slightly over the pertinent range of internuclear separations, indicating that effects in the continuum also contribute to the observations. Specifically, the scattering of the photoelectron into partial waves exhibiting Cooper minima is $R$-dependent, and is a manifestation of how the molecular potential experienced by the photoelectron mediates the coupling between electronic and photoion angular momenta.\(^1\)\(^2\)\(^3\) Both the initial and final state contributions are pertinent to the observed effects, and a more complete discussion will be provided elsewhere.\(^2\)\(^3\)

In conclusion, we have exploited Cooper minima to probe correlations between electronic, vibrational, and rotational motions in $2\sigma_u^{-1}$ photoionization of $\text{N}_2$. The results show clearly that $R$-dependent Cooper minima lead to a dependence of photoion rotational populations on the photoion vibrational level. Because Cooper minima are ubiquitous in molecular systems,\(^1\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\)\(^13\)\(^14\)\(^15\)\(^16\)\(^17\)\(^18\)\(^19\)\(^20\)\(^21\)\(^22\)\(^23\)\(^24\)\(^25\)\(^26\)\(^27\) such photoionization studies can be effective probes of vibrational--rotational--electronic correlations. Furthermore, the current study demonstrates the utility of dispersed fluorescence as a survey tool to complement electron spectroscopy. The current investigation also highlights a general theme that emerges from our previous work.\(^1\)\(^1\)\(^2\)\(^3\)\(^11\)\(^12\)\(^13\)\(^14\)\(^15\)\(^21\)\(^25\)\(^26\)\(^27\) Specifically, vibrationally and rotationally resolved aspects of molecular photoionization provide a means of \text{"dissecting\"} the angular momentum composition of the electronic continuum and of understanding microscopic aspects of the scattering dynamics, even when the unresolved cross sections are nearly featureless, as is the case in the current study.\(^2\)\(^3\) The key point is that probes which emphasize the molecular nature of the process, such as vibrationally and rotationally resolved methods, are naturally well-suited for elucidating the underlying dynamics.

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\(^6\)J. Guo, A. Mank, and J. W. Hepburn, Phys. Rev. Lett. \textbf{74}, 3584 (1995). However, the $2\sigma_u$ orbital composition evolves only slightly over the pertinent range of internuclear separations, indicating that effects in the continuum also contribute to the observations. Specifically, the scattering of the photoelectron into partial waves exhibiting Cooper minima is $R$-dependent, and is a manifestation of how the molecular potential experienced by the photoelectron mediates the coupling between electronic and photoion angular momenta.\(^1\)\(^2\)\(^3\) Both the initial and final state contributions are pertinent to the observed effects, and a more complete discussion will be provided elsewhere.\(^2\)\(^3\) In conclusion, we have exploited Cooper minima to probe correlations between electronic, vibrational, and rotational motions in $2\sigma_u^{-1}$ photoionization of $\text{N}_2$. The results show clearly that $R$-dependent Cooper minima lead to a dependence of photoion rotational populations on the photoion vibrational level. Because Cooper minima are ubiquitous in molecular systems,\(^1\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\)\(^13\)\(^14\)\(^15\)\(^16\)\(^17\)\(^18\)\(^19\)\(^20\)\(^21\)\(^25\)\(^26\)\(^27\) such photoionization studies can be effective probes of vibrational--rotational--electronic correlations. Furthermore, the current study demonstrates the utility of dispersed fluorescence as a survey tool to complement electron spectroscopy. The current investigation also highlights a general theme that emerges from our previous work.\(^1\)\(^1\)\(^2\)\(^3\)\(^11\)\(^12\)\(^13\)\(^14\)\(^15\)\(^21\)\(^25\)\(^26\)\(^27\) Specifically, vibrationally and rotationally resolved aspects of molecular photoionization provide a means of \text{"dissecting\"} the angular momentum composition of the electronic continuum and of understanding microscopic aspects of the scattering dynamics, even when the unresolved cross sections are nearly featureless, as is the case in the current study.\(^2\)\(^3\) The key point is that probes which emphasize the molecular nature of the process, such as vibrationally and rotationally resolved methods, are naturally well-suited for elucidating the underlying dynamics.

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