Electron-impact-induced transitions in molybdenum and their use in modelling of a moly-oxide discharge lamp

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Abstract. Theoretical results from multi-state non-relativistic R-matrix (close-coupling) calculations are presented for electron-impact-induced transitions between excited states of molybdenum. The results are then used in modelling a low-pressure mercury-free Ar-MoO₃ discharge lamp. Despite the complexity in the structure description of such an open-shell target and the resulting challenges in subsequent collision calculations, it is shown that an ab initio calculation can predict the most important kinetic pathways leading to the emission of visible and ultraviolet radiation. Satisfactory quantitative agreement, within approximately a factor of 2, is obtained between the measured and modelled spectra of the molybdenum-oxide discharge lamp.

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1. Introduction

One of the outstanding challenges in applied plasma physics is the development of non-mercury gas discharges for lighting. This objective is driven by environmental concerns of hazardous materials in landfills and evidenced by the proposed legislation within the European Union for collection and recycling of the material from spent lamps, such as automotive headlights, prior to disposal. To comply with this directive and anticipated ones for the United States, recent efforts in lighting research have focused on alternatives to Hg as (i) the primary UV emitter in standard fluorescent lamps with phosphor \[1, 2\] and (ii) the high-pressure buffer gas in metal-halide lamps [3, 4]. Another non-Hg lamp concept involves using high-vapour-pressure metallic compounds to directly generate white light from the collisional excitation of dissociated metal atoms in a low-pressure rare-gas buffer. This concept has been demonstrated at the Naval Research Laboratory using an inductive discharge to excite neutral molybdenum within a bulb loaded with MoO\(_3\) powder and backfilled with Ar at 1 or 2 Torr pressure [5].

In two recent papers [6, 7], we presented results for electron collisions with molybdenum atoms. The first paper [6] focused on elastic scattering and electron-impact excitation of molybdenum from the \((4d^55s)^7S\) ground state to a number of excited states, while these and other collision results were then used in studying the kinetic pathways to visible light emission from a moly-oxide-argon discharge bulb [7]. The purpose of the present paper is to present some of these additional results (a full set of data is available from the authors on request) and compare the measured and the modelled spectra from the discharge lamp. This comparison shows how \textit{ab initio} calculations for such a complex system as molybdenum can indeed be used to qualitatively predict such spectra and hence can serve to reliably determine the most important pathways to light emission in this and other types of lamps. The results presented can also be used in divertor studies in several experimental facilities, where a spectroscopic determination of impurity influx from the molybdenum surface is needed [8].

This paper is organized as follows. After a summary of the major computational challenges regarding the structure and the collision calculations, we will present results for the electron-induced cross sections along the most important pathways identified previously [7] that lead to visible light emission. This is followed by a comparison of the spectra from the lamp and our outlook regarding the future success of such combined computational and applied efforts to understand complex discharge physics.

2. Structure and collision calculations

Figure 1 shows the part of the MoI bound spectrum that is most relevant for the present work. Because of the enormous number of individual fine-structure levels, only the \(LS\)-terms are shown. The terminology is adopted from Sugar and Musgrove [9]. Most important for the discussion below are the 15 states in the septet and quintet ladders below an excitation energy of 4.5 eV. As can be seen from the figure, visible radiation predominantly originates from the quintet manifold, particularly the \(z^5F^o\), \(y^5P^o\), and \(z^5P^o\) states, all of basic configuration 4d\(^5\)5p. In addition, UV radiation is emitted from the \(y^7P^o\) and \(z^7P^o\) states, of the same configuration 4d\(^5\)5p, back to the ground state \(a^7S^e\) with configuration 4d\(^5\)5s. This latter radiation is undesirable for the visible light emission, and hence mechanisms to suppress energy losses into feeding these transitions need to be investigated [7]. It is also worth noting that the situation is much more complicated than it may
Figure 1. Simplified energy term spectrum of Mo I. The shadowed areas indicate the range covered by the various fine-structure levels of the $LS$ term listed. The quintet and septet states below an excitation energy of 4.5 eV are of primary interest for the present work.
appear from looking only at the principal configurations of these states, due to different internal couplings within the approximately half-filled 4d-shell. These different couplings result in a strong term dependence of the individual one-electron orbitals. In order to account for this term, dependence, at least to some extent, one typically needs to include so-called ‘pseudo-orbitals’ and use multi-configuration expansions in the description of the target states.

In the structure calculation described in detail in [6], the term dependence, indeed, turned out to be a major problem. A particular difficulty was associated with the 4d orbital, which is occupied by four, five or six electrons in the terms of interest. The problem was addressed by fine-tuning the choice of this orbital, starting the optimization procedure with the 4d orbital for the a5D state and supplementing two pseudo-orbitals, 6s and 5d, in addition to the physical 5p valence orbital. The latter was generated through energy optimization of the [4d5 (a6S)5p]z2P0 state.

Some indication of the quality of the target description is provided not only by the energies of the target states or, more accurately, the energy splittings between the target states, but also by the oscillator strengths or transition rates. Except for the [4d5 (a6S)5s]a7S → [4d45s (a6D)5p]y7Po transition, where the current model yielded a far too small oscillator strength that was ultimately adjusted to the experimental value of Whaling et al [10], the agreement between the results obtained with the length and the velocity forms of the dipole operator, as well as with experiment, was satisfactory given the complexity of the problem. Nevertheless, differences of up to a factor of two remained.

Using the target description discussed above, we then extended the work of Badnell et al [8] on this collision problem and performed several sets of collision calculations using the R-matrix (close-coupling) method as programmed by Berrington et al [11] inside the R-matrix boundary region and by Burke and Noble [12] in the outer region. These regions are defined by partitioning the configuration space into two regions by a sphere of radius \( r = a \), where \( r \) is the relative coordinate of the scattering electron and the centre of gravity of the target atom. This sphere is chosen to completely envelope the electronic orbitals of the target atom or ion. Hence, in the internal region \( r \leq a \), exchange and correlation effects between the scattering electron and target electrons must be included, whereas in the external region exchange effects can be neglected and the problem simplifies considerably.

In the internal region, the \((N + 1)\)-electron wavefunction at energy \( E \) is expanded in terms of an energy-independent basis set, \( \psi_k \), as

\[
\Psi_E = \sum_k A_{Ek} \psi_k.
\]

The basis states, \( \psi_k \), are expanded in the form

\[
\psi_k(x_1, \ldots, x_{N+1}) = A \sum_{ij} \tilde{\Phi}_i(x_1, \ldots, x_N; \tilde{r}_{N+1}(\sigma_{N+1})r_{N+1}^{-1}u_{ij}(r_{N+1})c_{ijk} + \sum_j \chi_j(x_1, \ldots, x_{N+1})d_{jk},
\]

where \( A \) is the antisymmetrization operator. The channel functions \( \tilde{\Phi}_i \) are obtained by coupling the orbital and spin angular momenta of the target states \( \Phi_i \) with those of the scattered electron to form eigenstates of the total orbital and spin angular momenta \( L \) and \( S \), their \( z \)-components \( M_L \) and \( M_S \) and the parity \( \pi \). The set of states \( \Phi_i \) includes both target eigenstates and possibly
pseudo-states. The $u_{ij}$ are members of a complete set of numerical orbitals used to describe the radial motion of the scattered electron and $\chi_j$ are $(N+1)$-electron configurations included to allow for short-range correlation effects between the scattered and target electrons and to ensure completeness of the expansion when orthogonality restrictions are imposed in generating the continuum basis. The coefficients $c_{ijk}$ and $d_{ij}$ are obtained by diagonalizing the $(N+1)$-electron Hamiltonian matrix in the internal region.

Each of the target eigenstates and pseudo-states is expanded in terms of a sum of orthonormal configurations

$$
\Phi_i(x_1, \ldots, x_N) = \sum_j \phi_j(x_1, \ldots, x_N) c_{ij},
$$

where the $\phi_j$ are constructed from a set of orthonormal one-electron orbitals, which can be either bound physical orbitals or pseudo-orbitals, included to represent electron correlation effects and sometimes the target continuum. In addition to the physical bound orbitals and the $6s$ and $5d$ pseudo-orbitals, we used a continuum basis generated by solving the differential equation

$$
\left(-\frac{1}{2} \frac{d^2}{dr^2} + \ell(\ell + 1) + V_0(r) - \frac{1}{2} k_{n\ell}^2\right) u_{n\ell}(r) = \sum_{n'} \lambda_{n'\ell} P_{n'\ell},
$$

subject to the boundary conditions

$$
u_n(0) = 0,
$$

$$
a \frac{du_n(r)}{dr} \bigg|_{r=a} = b.
$$

As is the usual practice, the arbitrary constant $b$ was set to zero and the zero-order potential $V_0$ was chosen as the ground-state potential of MoI. The Lagrange multipliers $\lambda_{n'\ell}$ are used to ensure orthogonality of the continuum basis to all the physical bound orbitals $P_{n'\ell}$ with the same orbital angular momentum $\ell$, i.e., 1s–5s, 2p–5p, and 4d–5d, and Gram-Schmidt orthogonalization was used to project out the overlap between the continuum basis and the $6s$ and $5d$ pseudo-orbitals. In all calculations, the $R$-matrix radius $a$ was set to $30a_0$ (with $a_0$ being the Bohr radius), and 25 continuum orbitals per angular momentum were included in the expansion. These numerical orbitals, together with the Buttle correction [13] to approximately represent the effect of the orbitals omitted from a complete continuum basis, ensured convergence of the results in this aspect for all our collision energies of interest. Finally, total orbital angular momenta up to $L = 13$ with all possible total spin channels (octet, sextet and quartet) coupled with the septet and quintet target states ensured convergence of the partial-wave expansion.

As mentioned above, we performed several sets of calculations, in which 15, 29, or 67 states were retained in the close-coupling plus correlation expansion. The 15-state model only included the lowest 15 septet and quintet states of MoI (see figure 1), while the 29-state approach contained the lowest 14 triplet states as well. Finally, the 67-state calculation coupled all septet, quintet, and triplet states with an energy below 7 eV with respect to the ground state. Since we were only interested in transitions between septet and quintet states, we omitted the singlet spin states completely, because they can only affect these results via coupling through several spin-changing transitions. Although not entirely free from the problem, the 67-state model...
is expected to be least affected by so-called ‘pseudo-resonances’. These structures occur due
to the presence of unphysical thresholds associated with states whose dominant configuration
involves one or more pseudo-orbitals and, even more importantly, due to a usually inconsistent
treatment of the $N$-electron target and the $(N + 1)$-electron collision problems. The latter problem
becomes particularly prominent if not all of the states that could be generated from the $N$-electron
configurations are kept in the close-coupling expansion. Since currently available computational
resources make it essentially impossible to retain all the 1350 target states, which could have
been generated from our $N$-electron configurations, compromises had to be made. As will be
illustrated below, one can nevertheless draw qualitative conclusions about the pseudo-resonance
problem by comparing the results from different models.

3. Cross-sections for the dominant pathways

In our earlier paper the modelling of the moly-oxide-argon discharge lamp [7] was detailed and
four important pathways leading to the emission of visible radiation were identified, namely

(a) $\text{Mo}(^7S^e) \rightarrow \text{Mo}(^7P^o) \rightarrow \text{Mo}(^5D^e) \rightarrow \text{Mo}(^5P^o) \rightarrow \text{radiation}$.

This path results in visible radiation with wavelengths 550–603 nm. The radiation in the
interval 550–557 nm is due to radiative decay from $\text{Mo}(^7P^o) \rightarrow \text{Mo}(^5S^e)$, while the radiation
between 560 and 603 nm arises from transitions $\text{Mo}(^7P^o) \rightarrow \text{Mo}(^5D^e)$. The former interval is
characteristic of Mo as it contains the strongest visible radiation emitted. Note that the second step
along this path corresponds to an electron-induced de-excitation, sometimes called ‘superelastic
scattering’. There is no threshold energy to overcome; instead, the projectile electron gains energy
by de-exciting the target.

(b) $\text{Mo}(^7S^e) \rightarrow \text{Mo}(^5S^e) \rightarrow \text{Mo}(^7P^o) \rightarrow \text{radiation}$.

This is an alternative channel for populating the $\text{Mo}(^7P^o)$ level. The competition between
channels (a) and (b) depends on the Mo pressure [7]. At low ground state density, the UV
emission from $\text{Mo}(^7P^o)$ to the ground state $\text{Mo}(^5S^e)$ depletes the resonance states and makes
the transfer from the septet to the quintet levels (channel a) inefficient compared to the emission
from the $^7P^o$ state directly pumped from the metastable $^5S^e$ state (channel b). For high ground
state density, on the other hand, channel (a) dominates over channel (b).

(c) $\text{Mo}(^7S^e) \rightarrow \text{Mo}(^5D^e) \rightarrow \text{Mo}(^5P^o) \rightarrow \text{radiation}$.

The excitation to the other metastable level, $\text{Mo}(^5D^e)$, is followed by further excitation to
$\text{Mo}(^5P^o)$ and subsequent radiative emission at 444–466 nm. The electron-impact excitation
rate coefficient for the transition $\text{Mo}(^5D^e) \rightarrow \text{Mo}(^5P^o)$ is smaller by one order of magnitude
compared to that for $\text{Mo}(^5S^e) \rightarrow \text{Mo}(^5P^o)$. This explains why the line intensities in the 444–
466 nm interval are much smaller than the line intensities originating from $\text{Mo}(^7P^o)$ level [7].

(d) $\text{Mo}(^7S^e) \rightarrow \text{Mo}(^5D^e) \rightarrow \text{Mo}(^5F^o) \rightarrow \text{radiation}$.

This excitation path is similar to channel (c) and gives rise to visible radiation at wavelengths
$\lambda \sim 430$ nm.

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Figure 2. Cross-sections for electron-induced transitions between $^7$S$^e \rightarrow ^7$P$^o$ (top panel), $^7$P$^o \rightarrow ^5$D$^e$ (middle panel), and $^5$D$^e \rightarrow ^5$P$^o$ (bottom panel) as a function of the incident electron energy. These transitions correspond to path (a) described in the text. The various numerical models are labelled according to the number of states included in the close-coupling plus correlation expansion.

Figures 2–4 exhibit our cross-section results for electron-induced transitions along the four pathways listed above. In general, the cross-sections for transitions between excited states are much larger than those for excitation from the ground state. Also, the spin-changing transitions peak at very low incident electron energies. The strong energy dependence exhibited in these curves shows the importance of choosing the proper electron temperature to optimize the discharge lamp.
Figure 3. Cross-sections for electron-induced transitions between $a^7S \rightarrow a^5S$ (upper panel) and $a^7S \rightarrow z^5P^0$ (lower panel) as a function of the incident electron energy. These transitions correspond to path (b) described in the text. The various numerical models are labelled according to the number of states included in the close-coupling plus correlation expansion.

Looking at the various theoretical models in more detail, we notice the satisfactory trend of diminishing pseudo-resonance effects when going from the 15-state to the 67-state model. Also, for these relatively large cross-sections, the similarity of the 29-state and the 67-state results indicates a reasonable convergence of the close-coupling expansion, i.e., one may conclude that the most important channel-coupling effects have, indeed, been accounted for. A further improved structure description would, of course, be desirable, but the present results can already be expected to reflect the most important aspects of these electron-induced transitions.

4. Comparison of the spectra

Figure 5 shows an actual spectrum from a moly-oxide-argon discharge lamp, obtained with an argon pressure of 2 Torr, a radiofrequency (RF) input power of 200 W and an effective radius
Figure 4. Cross-sections for electron-induced transitions between \(a^7S^e \rightarrow a^5D^e\) (top), \(a^3D^e \rightarrow y^2P^o\) (bottom left), and \(a^3D^e \rightarrow z^3F^o\) (bottom right) as a function of the incident electron energy. These transitions correspond to paths (c) and (d) described in the text. The various numerical models are labelled according to the number of states included in the close-coupling plus correlation expansion.

Figure 5. Spectrum from a molybdenum-oxide lamp. The discharge conditions were: \(p_{\text{Ar}} = 2\) Torr, \(P_{\text{RF}} = 200\) W and \(R = 1.3\) cm.
Figure 6. Measured (upper panel) and modelled (lower panel) MoI lines in a moly-oxide discharge lamp.

$R = 1.3 \text{ cm}$ of the plasma volume. Note that some of the lines originate from atoms other than excited neutral molybdenum, in particular from neutral argon and oxygen in the infra-red regime and from singly ionized molybdenum in the ultraviolet. As mentioned previously, the $\gamma^7P^o \rightarrow a^7S^e$ and $\gamma^7P^o \rightarrow a^7S^e$ transitions in neutral molybdenum also lead to strong UV radiation with wavelengths $313–317$ and $380–390 \text{ nm}$, respectively. In order to improve the visible-light efficiency of the lamp, this UV radiation could either be converted into the visible domain by using specialized phosphor or suppressed by increasing the Mo ground state density [7]. In the latter case, the increased trapping of the resonance transition would lead to quenching of the UV radiation.

In figure 6, dominant lines from neutral molybdenum are presented, providing a qualitative comparison between the measured (top) and the modelled (bottom) line spectra. Table 1 lists the line intensities from the figure arranged by groups, along with the wavelength range for each group. We first note that the powers from the model calculation are often larger (by up to a factor of two) than the observed data. One possible explanation is that the density of Mo atoms, $1.2 \times 10^{13} \text{ cm}^{-3}$, is overestimated in the model. This density is taken from figure 10 of [7] and is based on a plasma kinetics model for the cycling of molybdenum atoms: bulb wall evaporation.
Table 1. Molybdenum line intensities by group from experiments and modelling.

| Group  | Wavelength range (nm) | Line intensity |
|--------|----------------------|----------------|
|        | Experiment (mW cm⁻² st⁻¹) | Ratio | Model (mW cm⁻² st⁻¹) | Ratio |
| y⁷P–a⁷S | 313–320              | 19.5 | 1.26 | 21.8 | 0.72 |
| z⁷D–a⁷S | 311–320              | 9.2  | 0.59 | 17.6 | 0.58 |
| z⁵P–a⁷S | 345–347              | 3.9  | 0.25 | 1.5  | 0.05 |
| z⁷P–a⁷S | 380–390              | 22.2 | 1.43 | 36.6 | 1.21 |
| y⁷F–a⁵D | 427–429              | 8.0  | 0.52 | 12.1 | 0.40 |
| y⁵P–a⁵D | 462                  | 1.2  | 0.08 | 1.4  | 0.05 |
| y⁷D–a⁵S | 478–498              | 0.6  | 0.04 | 2.5  | 0.08 |
| y⁵P–a⁵S | 550–557              | 15.5 | 1.00 | 30.3 | 1.00 |
| z⁵P–a⁵D | 588–603              | 4.9  | 0.32 | 6.1  | 0.20 |

as a molecule (MoO₃); impact dissociation in the plasma; metal recondensation on the wall; and wall recombination with oxygen producing MoO₃. The dissociation rates for this complex process are practically unknown and hence had to be estimated in the model. Furthermore, it is likely that too few radiative transitions were included in the model. The total visible radiation from the model matches the data; it is therefore likely emitted in fewer and more intense lines than in the actual experiment.

Table 1 also lists the ratio of intensities normalized to that from the z⁵P–a⁵S group for both the experimental data and the model. Except for the z⁵P–a⁷S group, the ratios are fairly consistent between the experiment and the model. This indicates that the relative populations of the quintet and septet levels are correctly produced by the electron excitation cross-sections calculated in this paper.

Heavy-particle collisions between Ar and excited Mo were neglected in our kinetics model. Although this specific reaction is not known, typical values for the collision constant of the same reaction between excited Hg and Ar are \( \sim 1 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \) [14]. For Ar at 2 Torr, this yields a collision rate of \( \sim 10^4 \text{s}^{-1} \). Electron collision constants between a septet and a quintet level are \( \sim 10^{-8} \text{ cm}^3 \text{s}^{-1} \), as calculated, for example, from the results presented in the middle panel of figure 2 for a typical speed distribution. Both the measured [5] and the model [7] values for the electron density are \( 2 \times 10^{13} \text{ cm}^{-3} \). Hence, heavy-particle collisions can be neglected compared to electron kinetic processes.

The relative intensities shown in the lower panel of figure 6 within each group were calculated by weighting each component by its statistical weight from [9]. These appear to be fairly consistent with the data in the upper panel. Although the agreement is by no means perfect, figure 6 and table 1 show that the present ab initio calculation provides the essential information about the electron-induced physics of the discharge lamp. Analysing the results from the calculation proved to be a very useful tool in determining the important pathways for generating visible light, and also to identify critical loss mechanisms.

5. Conclusions

We have presented selected results for electron-impact-induced transitions in molybdenum. A full set of cross-section data for transitions between the lowest 15 septet and quintet states...
displayed in figure 1 is available in numerical form from the authors upon request. Furthermore, the relevant rate coefficients can be found in table II of [7]. In a subsequent step, these results were used to determine the important kinetic pathways leading to emission of visible and ultraviolet radiation in a molybdenum-oxide discharge lamp. The satisfactory agreement obtained between the measured and predicted spectra of the lighting discharge represents a showcase for the fruitful interaction between the production and application of atomic data. With the rapid advances in computational resources and the corresponding software, particularly for large parallel environments, we expect an ever increasing role of ab initio calculations to provide essential input for modelling efforts in plasma chemical kinetics.

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